THE ELECTRONIC SPECTRA
OF
THE HALIDES OF TIN AND SILICON

P. R. K. SARMA

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The thesis entitled " The Electronic Spectra of the Halides of Tin and Silicon " has been divided into four chapters and the abstracts of these chapters are given below:

Chapter I: The emission spectrum of Tinmonochloride.

Stannic chloride vapour has been excited by uncondensed transformer discharge in the presence of argon. A new band system has been obtained in the region 6400-4800A. A large number of new bands were obtained in the 4000-3400A system which was known earlier. These systems as well as the another known system in the region 3400-2800A were photographed in the 1st and 2nd orders of a Jarrel Ash Ebert mounting 3.4 metre grating spectrograph. The vibrational constants obtained for the new system and the modified vibrational constants of the known system are

System	ν_0.cm^{-1}	ω_e' cm-1	$\omega_e'x_e'$cm-1	ω_e'' cm^{-1}	$\omega_e''x_e''$cm^{-1}
6400-4800A	19354	232.8	0.9	347.4	0.7
4000-3400A	28666	300.8	4.0	353.6	1.2
	26580	303.3	3.7	354.3	1.0
3400-2800A	33625	432.5	1.2	353.6	1.2
	31264	432.5	1.2	354.3	1.0

Chapter II: Emission spectrum of tinmonobromide.

A new band system in the region 6400-5100A has been obtained by exciting stannic bromide vapour in the presence of argon with an uncondensed transformer discharge. The spectrum was photographed on the first order of the 3.4 metre grating spectrograph. Isotopic shifts due to tin and bromine were observed for some of the bands. The vibrational constants derived from the a analysis of this system are:in cm^{-1}:

ω_e' = 164.1, ω_e'' 247.08,
$\omega_e'x_e'$ = 0.9 $\omega_e''x_e''$ 0.48.

Chapter III: Emission spectrum of SiCl.

A new band system in the region 6200-4700A has been obtained by exciting the silicon tetrachloride vapour in the presence of argon. The spectrum was photographed on Carlzeiss three prism glass spectrograph and also on the 1st order of a 3.4 metre grading spectrograph. The band system is analysed and is anologous to the new sytems of SiCl and SnBr. Further, the band system in the region 3200-2850A reported by earlier workers is photographed in the 2nd order of the grating spectrograph in which a large number of new bands are obtained. The vibrational constants of the new system and the improved vibrational constants of the known system are in cm^{-1}:

System	ν_{00}	ω_e'	$\omega_e'x_e'$	ω_e''	$\omega_e''x_e''$
6200-4700A	20900	297.4	1.1	519.4	2.1
3200-2830A	33978.3 34184.5	707.8	4.7	534.4	2.1

Chapter IV: The electronic term scheme and the stable electronic states of SiF, SiCl, SnCl and SnBr.

The electronic term scheme of the halides of silicon and tin is discussed. Electronic configurations are tentatively assigned to the various observed electronic states of SiF, SiCl, SnCl and SnBr. The different stable electronic states of these molecules are listed along with their vibrational constants.

THE ELECTRONIC SPECTRA
OF
THE HALIDES OF TIN AND SILICON

P. Radha Krishna Sarma, M. Sc. (Benaras)

Thesis submitted in partial fulfilment of
the requirements for the award of the
degree of Doctor of Philosophy of
Muslim University, Aligarh.
1961.

Certified that the work described in this thesis is the original work of Mr. P.R.K. Sarma, done under my supervision.

P. Venkateswarlu

(P. Venkateswarlu)

Department of Physics,
Muslim University,
ALIGARH.

PREFACE

The thesis deals with the emission spectra of SnCl, SnBr and SiCl obtained by exciting the respective tetra halides in the presence of argon.

Chapter I concerns with the spectrum of SnCl and is divided into four sections. A band system in the region 6400-4800A, discussed in section A, is recorded for the first time and the analysis proposed for this system has been well supported by the observed isotopic shifts due to chlorine. The band systems discussed in sections B and C are reported by earlier workers but a large number of new bands are observed in the present experiments. As the ground state is involved in both these systems, a set of common vibrational constants are derived from the re-analyses of both these systems. The absorption data obtained by earlier workers are given in Section D and it is shown that it can also be well explained with the help of the ground state constants derived in sections B and C.

Chapter II deals with a new band system attributed to SnBr in the region 6400-4800A. The validity of the proposed vibrational analysis has been well supported by the observed isotopic shifts due to tin and bromine.

The analysis of a new band system of SiCl in the region 6200-4700A and the analysis of the known band system in the region 3200-2850A, taken on a higher dispersion instrument, (thereby deriving better vibrational constants) form the third Chapter.

The probable electronic configurations and electronic states involved in various systems of SiF, SnCl, SnBr and SiCl are discussed in Chapter IV.

Most of the work described in the thesis has been carried out in the department of Physics, Muslim University, Aligarh. The spectra with 3.4 meter grating spectrograph were photographed with the instrument in the Chemistry division, Atomic Energy Commission Bombay, with the kind permission of Professor R. K. Asundi.

All the work described in the thesis has been done by me under the guidence of Dr. Putcha Venkateswarlu, Department of Physics, Muslim University, Aligarh. I wish to express my indebtedness and thanks to Dr. Venkateswarlu for his guidence and encouragement during the course of the development of this work. Thanks are due to Prof. R.K. Asundi and Dr.N.A. Narasimham for their valuable suggestions during my brief stay at Bombay. I sincerely thank Mr. D. Ramakrishnan for the hospitality shown to me during the period of my stay

at Bombay. I am earnestly thankful to Professor P. S. Gill for his kind interest during the course of this work and to the U.P. Government Research Committee for a research assistantship during a part of my stay at Aligarh.
Finally I have pleasure to express my warm thanks to all of my colleagues and friends for their constant encouragement and cooperation and to the technical staff of the Physics Department for their help during the development of this work.

CONTENTS

CHAPTER I

The Emission Spectrum of Tin MonoChloride

ABSTRACT

Stannic chloride vapour has been excited by an uncondensed transformer discharge in the presence of argon. A new band system has been obtained in the region 6400-4800A. A large number of new bands were obtained in the 4000-3450A system which was known earlier. These systems as well as the another known system in the region 3400-2800A were photographed in the first and second orders of a Jarrel Ash Ebert mounting 3.4 meter grating spectrograph. The vibrational constants obtained for the new system and the modified vibrational constants of the known systems are

System	ν_{oo} cm^{-1}	ω_e' cm^{-1}	$\omega_e'x_e'$ cm^{-1}	ω_e'' cm^{-1}	$\omega_e''x_e''$ cm^{-1}
6400-4800A	19354	232.8	0.9	347.4	0.7
4000-3450	28666	300.8	4.0	353.6	1.2
	26580	303.3	3.7	354.3	1.0
3400-2800A	33625	432.5	1.2	353.6	1.2
	31264	432.5	1.2	354.3	1.0

INTRODUCTION

Jevons[1] excited stannic chloride vapour by an uncondenced transformer discharge and recorded (i) two groups of discrete bands in the region 3900-3400A degraded to longer wavelengths (ii) two other groups of bands in the region 3400-2800A degraded to shorter wavelengths and (iii) two strong continua with the intensity maxima at 5100A and 2600A. All the four groups of bands mentioned above have also been observed by Ferguson[2] by exciting stannic chloride vapour in a stream of active nitrogen. Besides the above groups of discrete band systems, a group of diffuse bands were obtained later by Asundi, Karim and Samuel[3] in the region 4800-4550A by exciting $SnCl_2$ vapour in condensed and uncondensed transformer discharge and were attributed to $SnCl_2$ molecule. Fowler[4] studied the absorption spectrum of SnCl obtained by heating $SnCl_2$ vapour upto 1200°c or 1300°c and reported the occurance in absorption of (1) the higher frequency groups of the two band systems obtained earlier in emission by Jevons and Ferguson in the regions 3900-3400A and 3400-2800A (2) a new band system in the region 2450-2250A and (3) two continua in the regions 3500-3000 A and 2500-1900A.

The two groups of bands in the region 3400-2800A were classified by Jevons[1] as due to a transition from $a\,^2\Sigma$ state to the $^2\pi$ ground state of the SnCl molecule, the doublet separation being 2360 cm^{-1}. The other two groups of bands in

the region 3900-3400A obtained by exciting the $SnCl_4$ vapour in active nitrogen were analysed by Ferguson[2] as due to a transition from upper $^2\Delta$ state to the same $^2\pi$ ground state, $^2\Delta$ having a separation of 273.9 cm^{-1}. Even though the lower state of these two systems is one and the same the vibrational constants derived from the analysis of these two systems are different.

It was felt that the vibrational constants of the ground state could be improved if these systems are taken on a spectrograph having higher dispersion and higher resolution than those used by earlier workers. Accordingly the two systems were photographed in the first and second orders of a Jarrel Ash Ebert mounting 3.4 meter grating spectrograph and the results are discussed in sections B and C of this Chapter.

Halogen and mixed halogen molecules, when excited in the presence of argon are known to develop new discrete band systems in the place of continua or diffuse groups of bands that one gets by exciting those molecules without the presence of a foreign gas. Therefore it was felt that similar excitation of $SnCl_4$ in the presence of argon might develop new discrete band systems. A band system obtained by this method of excitation is discussed in section A of this Chapter.

Experimental Details

$SnCl_4$ vapour was excited in presence of argon by an uncondensed transformer discharge. The discharge tube was ⌐ shaped and was made of pyrex glass of 30 cms in length and 0.8 cm in diameter. Nickel electrodes were used in general but however the band systems obtained were checked also by using alluminium, tungsten and stainless steel electrodes. Argon marked spectrally pure was obtained from "Farbmerke Hoechst A.G." in one litre glass cylinders. $SnCl_4$ marked as laboratory reagent obtained from British Drug House was used without any further purification.

Little quantities of argon and stannic chloride vapour were allowed to pass into the discharge tube and the mixture was excited with 0.75 K.W. Hilger transformer. It was found out that with the increase of the pressure of argon the continuum in the visible region goes down in intensity and a new discrete band system appears in its place. By adjusting the pressures of argon and stannic chloride it is possible to decrese the intensity of the continuum and increase the intensity of the new band system. The pressure of argon or stannic chloride was not measured in the present experiments but it was estimated that the pressure of argon was many times higher than its counterpart. It was found out that when the new band system was intense, the discharge was bluish red in colour and tape-like in shape. Thus the shape and the

colour of the discharge acted in a way as a guide for maintaining the relative pressures of the two gases for obtaining the new system. It was found necessary to cool the discharge tube with the help of the table fans arranged on either side of the discharge tube to maintain the proper condition of the discharge for a longer time. Whenever the longer exposures were needed fresh samples of argon and stannic chloride were let in at regular intervals after pumping out the old mixture. It was observed that when the new band system developed with good intensity, the intensity of the known band systems also increased. The spectrum that was obtained with the present experimental conditions consists of

1. A new band system in the region 6400-4800A.
2. two groups of bands in the region 4000-3450A.
3. two groups of bands in the region 3400-2800A.

The band systems 1, 2 and 3 will be discussed in sections A, B and C respectively. The absorption band system in the region 2450-2250A obtained by Fowler[4] will be discussed in section D.

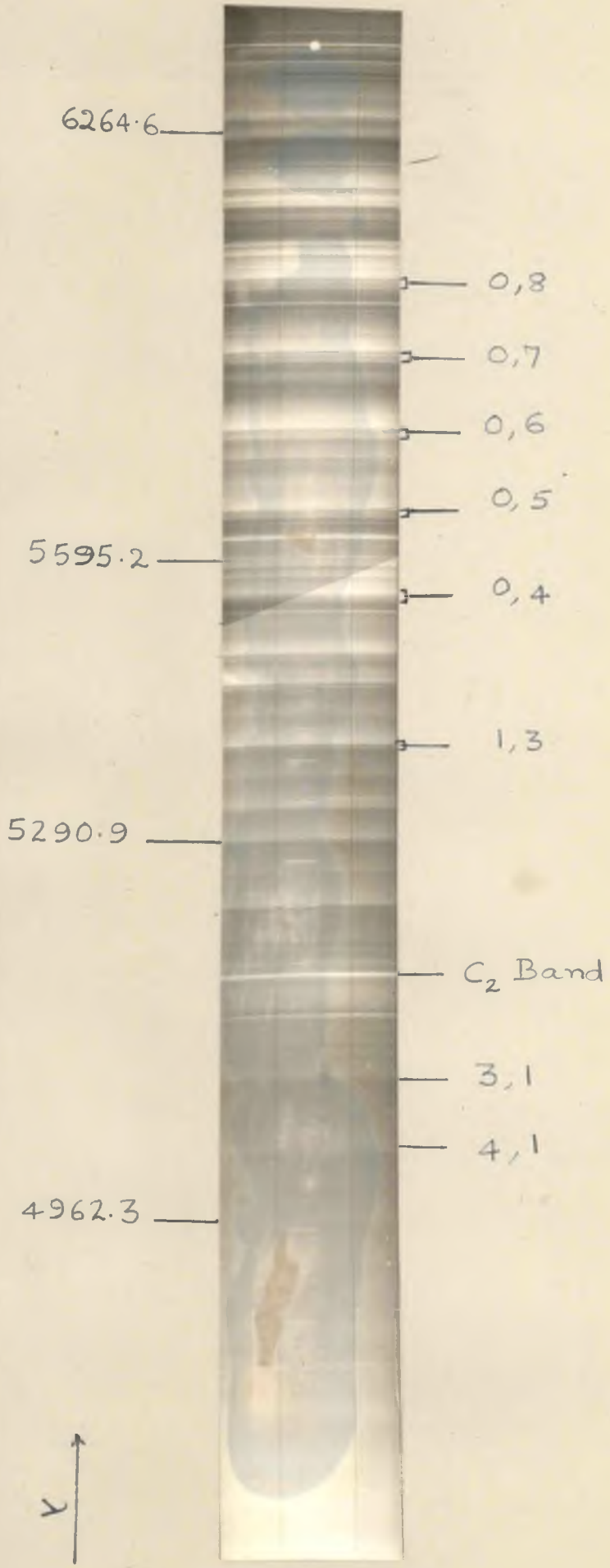

Fig. 1. The enlargement of 6300–4900A system of SiCl taken on Hilger spectrograph.

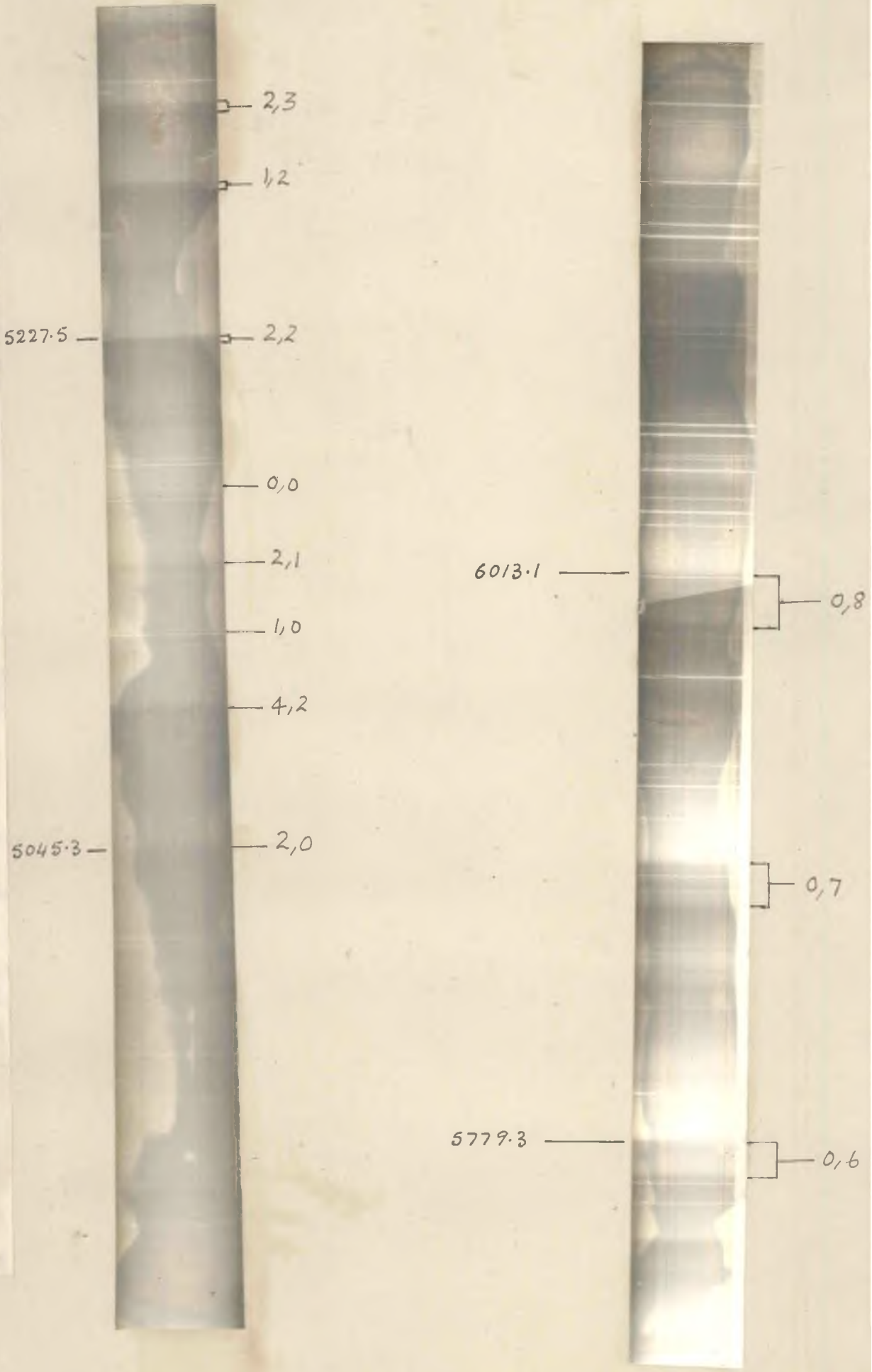

Fig. 2. The Enlargement of 6400–5000 system of SnCl taken on the grating Spectrograph.

SECTION A.

The new band system in the region 6400-4800A.

This band system, which developed only when the $SnCl_4$ vapour was excited in the presence of argon, was first photographed on a carlzeiss 3 prism glass spectrograph, the dispersion being 15A/m.m at 5400A. Fig. 1 shows the enlargement of the band system taken on the above-mentioned spectrograph. The spectrum was later photographed in the 1st order of a Jarrel Ash Ebert mounting 3.4 meter grating spectrograph with a dispersion of 5A/m.m. The time of exposure needed was only 20 minutes as the grating was blazed at 5000A in the first order. Fig.2 shows the enlargement of the band system taken on the grating spectrograph.

The wavelengths and wavenumbers of the $SnCl^{35}$ band heads measured with a Carl-zeiss Abbe comparator are given in table I along with their visually estimated relative intensities. The Deslandres scheme for the band system is given in table II. The intensity distribution according to the present analysis is of the form that is expected for a transition involving the observed ω_e' and ω_e'' values. All the bands observed could be well represented by the formula

$$\nu = 19354 + 231.9\,v' - 0.9\,v'^2 - 346.7\,v'' + 0.7\,v''^2$$

As the error involved in the measurements is estimated to be not more than ± 1.0 cm^{-1} the lower state of this transition is not likely to be the same as the lower state that is

TABLE I

Experimental data and assignment of $SnCl^{35}$ band heads of 6400-4800 system.

Wavelength λ_{air} in A	I	Wavenumber ν_{vac} in cm^{-1}	Assignment v' , v"	O - C in cm^{-1}
6398.1	0	15625	0 , 11	0
6305.1	1	15856	1 , 11	0
6264.6	2	15958	0 , 10	+1
6175.2	0	16189	1 , 10	+1
6136.4	3	16291	0 , 9	+0.6
6050.1	1	16524	1 , 9	+1.6
6013.1	4	16626	0 , 8	+0.8
5930.9	0	16856	1 , 8	-0.2
5893.9	4	16962	0 , 7	+0.4
5850.7	1	17087	2 , 8	+1.6
5814.6	0	17193	1 , 7	+0.6
5779.3	4	17298	0 , 6	-1.0
5739.1	2	17420	2 , 7	-1.6
5703.1	1	17529	1 , 6	-1.0
5668.3	4	17637	0 , 5	-1.0
5595.2	1	17868	1 , 5	-1.0
5561.1	5	17977	0 , 4	-1.6
5524.3	2	18097	2 , 5	-1.2
5490.4	10	18209	1 , 4	-0.6
5457.1	7	18320	0 , 3	-0.2

Table I contd.

Wavelength λ_{air} in Å	I	Wavenumber ν_{vac} in cm^{-1}	Assignment v' , v"	O - C in cm^{-1}
5422.3	3	18437	2 , 4	-1.6
5389	6	18551	1 , 3	-0.2
5356.5	3	18664	0 , 2	+0.6
5323.2	4	18780	2 , 3	-0.4
5290.9	4	18895	1 , 2	+0.6
5259.6	1	19008	0 , 1	0
5227.5	4	19124	2 , 2	+0.4
5196.1	1	19240	1 , 1	+1.0
5165.1	1	19354	0 , 0	0
5134.9	0	19469	2 , 1	+0.8
5106.5	0	19577	1 , 0	0
5104.5	0	19585	4 , 2	+0.6
5075.4	1	19697	3 , 1	+1.4
5045.3	0	19805	2 , 0	+0.8
5018.3	1	19922	4 , 1	+0.8
4988.2	0	20042	3 , 0	+0.4
4962.3	1	20146	5 , 1	+1.0
4932.4	0	20268	4 , 0	+0.8
4878.5	0	20492	5 , 0	+1

TABLE II

DESLANDRE'S SCHEME FOR THE 6400-4800 SYSTEM OF SnCl.

v'' / v'	0	1	2	3	4	5	6	7	8	9	10	11	$\Delta G'(v+1/2)$ Obs.	$\Delta G'(v+1/2)$ Col.
0	346 19354	344 19008	344 18664	343 18320	340 17977	339 17637	336 17298	336 16962	335 16626	333 16291	333 15958	15625	↓	↓
	231	232	231	231	232	231	231	231	230	233	231	231	231·3	231·0
1	345 19585	345 19240	344 18895	342 18551	341 18209	339 17868	336 17529	337 17193	332 16856	335 16524	333 16189	15856		
	230	229	229	229	228	229		227	231				229	229·2
2	346 19815	345 19469	344 19124	343 18780	340 18437	18097		333 17420	17087					
	227	228											227·5	227·4
3	345 20042	19697												
	226	225											225·5	225·6
4	346 20268	344 19922	19578											
													224	223·8
5	346 20492	20146												
	345·7	344·5	344	342·7	340·3	339	336	336·5	333·5	334	333	←	$\Delta G''(v+1/2)$ Obs.	
	346·0	344·6	3432	341·8	340·4	339	337·6	336·1	334·7	333·3	331·9	←	$\Delta G''(v+1/2)$ Col.	

involved in the other two ultraviolet systems, though the vibrational constants are close to one another. This supposition is also supported by the fact that no other sub-system has been observed either on low or high frequency side of this system which should have been probably obtained if the lower state of the new system is the same as the lower state of the ultraviolet systems. None of the electronic states involved in this transition could be identified with the known electronic states of the SnCl molecule. As the intensity of the ultraviolet band systems increased considerably when the present band system is well developed it is felt that it is likely that the emitter of the present system is also SnCl. If the emitter of the present system is the SnCl molecule the transition involved may probably be of $^2\Sigma \rightarrow ^2\Sigma$ type, as this system involves only single group of bands and as the rotational structure is relatively more open than that of the other two known systems which very likely involve the transition $^2\Sigma \rightarrow ^2\pi$ and $^2\Delta \rightarrow ^2\pi$. However nothing definite can be said about the electronic transition involved without carrying out the rotational analysis and the probability that this system might be due to $SnCl^+$ cannc also be ruled out without such an analysis. The bands were not well resolved to enable any useful rotational analysis to be carried out.

Isotopic effect

As the natural abundance ratio of Cl^{37} and Cl^{35} is 1:3 each $SnCl^{35}$ band should have a corresponding $SnCl^{37}$ band with one third of its intensity. The isotopic shifts due to tin isotopes are expected to be small* and are therefore not observed. The isotopic heads due to $SnCl^{37}$ can be seen in Fig. 1 and 2 in which they are marked as such. None of the band heads attributed to $SnCl^{37}$ could go into the vibrational scheme of $SnCl^{35}$ band heads. The observed isotopic shifts are listed in table III along with the corresponding calculated values. The close agreement between the observed and calculated isotopic displacements proves the emitter as SnCl (or $SnCl^{+}$) and it also proves the correctness of the assignment of vibrational quantum numbers.

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* The isotopic shifts for the longer wavelength bands are sufficiently large but owing to the low intensity they have not been observed.

TABLE III

Isotopic Displacements of 6400 - 4800A system.

$\nu_{vac}^{Sn^{37}Cl}$ in cm^{-1}	$\nu_{vac}^{Sn^{35}Cl}$ in cm^{-1}	)v' , v"	$(\nu' - \nu)$Obs	$(\nu' - \nu)$Cal
16682	16626	0 , 8	56	56.3
17012	16962	0 , 7	50	49.7
17132	17087	2 , 8	45	46.9
17340	17298	0 , 6	42	43.
17461	17420	2 , 7	41	40.2
17673	17637	0 , 5	36	36.3
17900	17868	1 , 5	32	31.5
18007	17977	0 , 4	30	29.4
18123	18097	2 , 5	26	26.8
18231	18209	1 , 4	22	24.6
18457	18437	2 , 4	20	19.9
18569	18551	1 , 3	18	17.9
18679	18664	0 , 2	15	15.5
18793	18780	2 , 3	13	13.
18905	18895	1 , 2	10	10.9
19130	19124	2 , 2	6	6
19244	19240	1 , 1	4	3.6

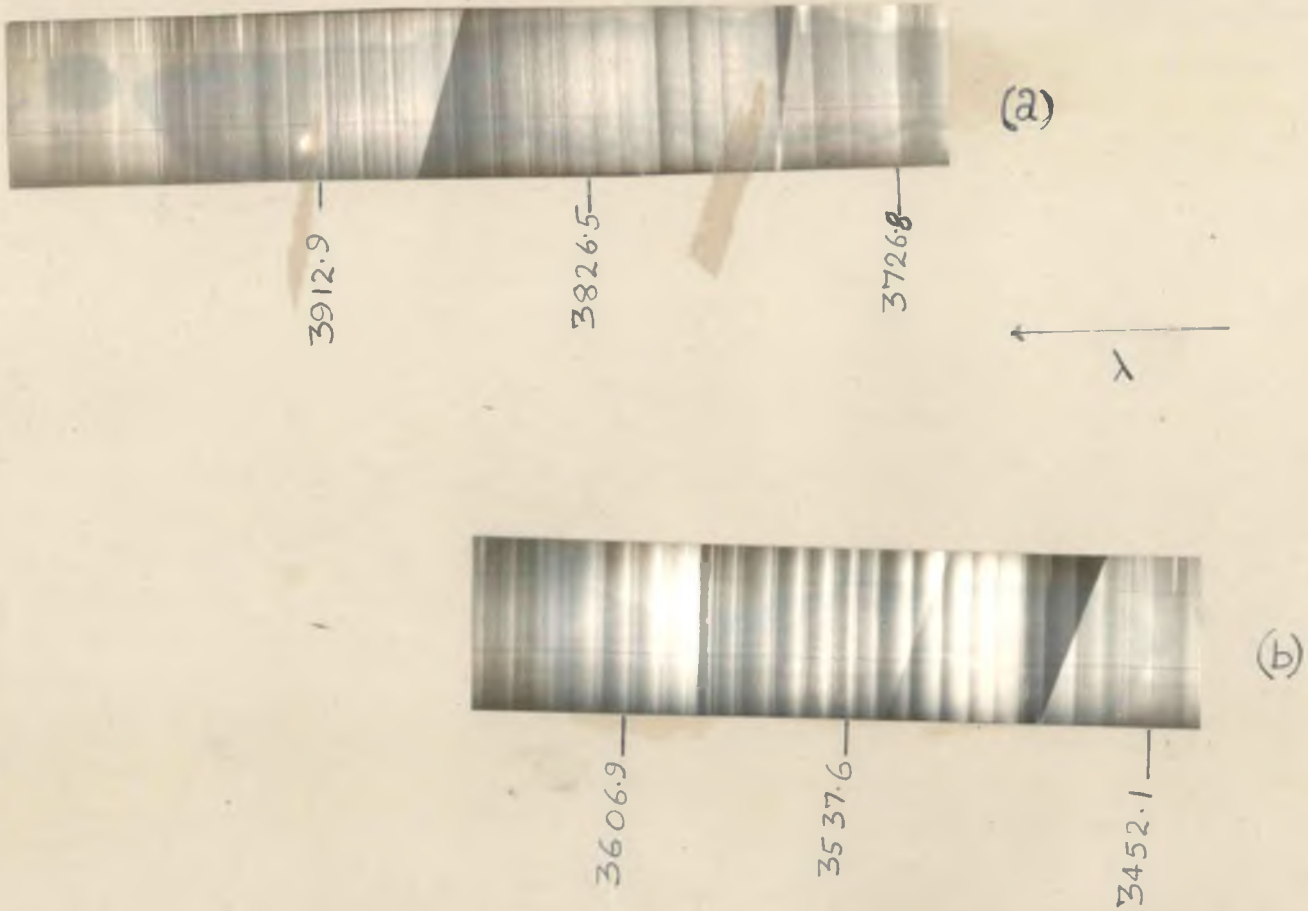

Fig. 3. The enlargement of 4000-3450A system of SnCl taken on the first order grating spectrograph
a. 4000-3700A (3800 group)
b. 3650-3450A (3500 group)

Fig. 4 The enlargement of 4000-3450A system of SnCl
taken on the second order of grating Spectrograph.
(a) 4000-3700A. (3800 group)
(b) 3650-3450A (3500 group)

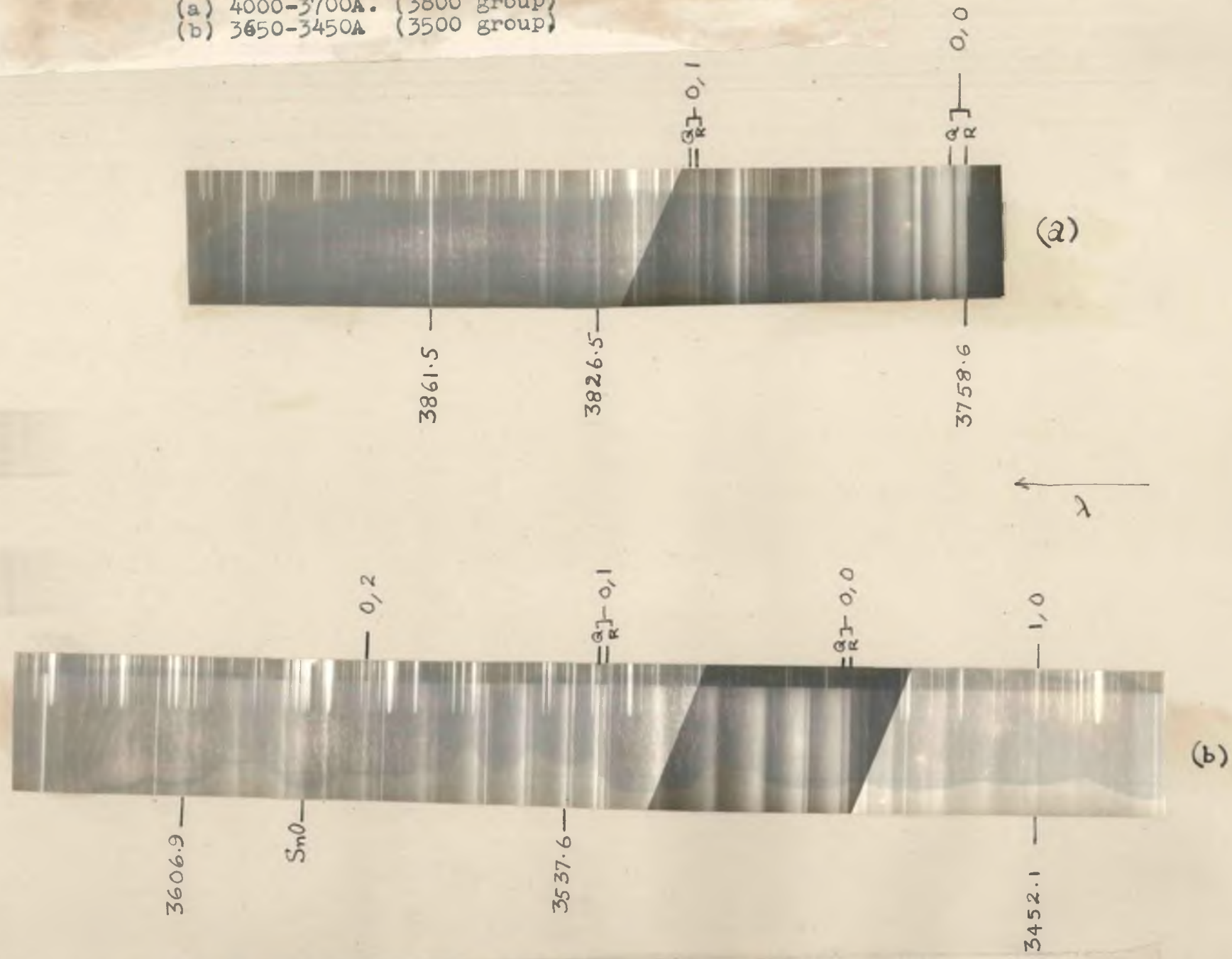

Fig. 4. The enlargement of 4000-3450A system of SnCl taken on the second order grating Spectrograph.

a. 4000-3700A (3800 group) b. 3650-3450A (3500 group)

SECTION B

The band system in the region 4000-3450A.

The band system in the region 3915-3480A originally reported by Jevons[1] and later worked out by Ferguson[2] on a prism spectrograph by exciting the $SnCl_4$ vapour in a stream of active nitrogen, is now photographed on the 1st and 2nd orders of the 3.4 meter grating spectrograph by exciting the molecule in presence of argon. As the intensity of the band system increased considerably by exciting the molecule in the presence of argon it was possible to photograph the system on Kodak B_{20} plates with the exposure times of 15 minutes and 2 hours in the first and second orders respectively. The dispersion of this grating spectrograph is 5A/m.m in the first order and 2.5A/m.m in the second order. A large number of new bands were obtained in this method of excitation and the spectrum is now extended to the region 4000-3450A. It was also possible to measure those bands which were masked by CN in the plates of earlier workers as there was no trace of CN bands in the present experiment. Fig 3 and 4 show the enlargements of the band system in the 1st and 2nd orders. All the bands in general show Q heads and R heads. The wavelengths and wavenumbers of the R and Q heads of $SnCl^{35}$ bands measured in the present experiments are given in table IV & V in which Ferguson's data are also include for comparison. As the band heads are very sharp the error in the present measurements is estimated to be probably not more

TABLE IV

Experimental data and the assignment of $SnCl^{35}$ band heads in the region 3950-3700A.

Ferguson ν_{vac} in cm^{-1}	I	Present Experiments λ_{air} A.U.	Present Experiments ν_{vac} in cm^{-1}	Assignment v' , v"	O - C in cm^{-1}
	1	3941.7	Q 25363	3 , 6	+0.4
	0	3940.5	R 25370		
	0	3932.3	Q 25423	2 , 5	+0.1
	0	3931.1	R 25431		
	0	3923.5	Q 25480	1 , 4	+1.3
	0	3922.0	R 25490		
	0	3916.0	Q 25529	0 , 3	-0.1
R25547	2	3912.9	R 25549		
	0	3899.5	Q 25636	4 , 6	-0.6
R25647	2	3898.1	R 25646		
	1	3889.2	Q 25706	3 , 5	+0.3
R25718	3	3888.4	R 25710		
	1	3879.7	Q 25768	2 , 4	+0.8
	3	3878.5	R 25776		
	0	3871.0	Q 25826	1 , 3	+1.0
	2	3869.6	R 25835		
	1	3863.2	Q 25878	0 , 2	+0.6
	2	3861.7	R 25835		
	1	3863.2	Q 25878	0 , 2	+0.6
	2	3861.7	R 25888		
	1	3848.5	Q 25977	4 , 5	+0.3
R25989	1	3847.5	R 25984		
	0	3837.7	Q 26050	3 , 4	-1.1
R26060.5	3	3836.1	R 26061*		
	1	3828.3	Q 26114	2 , 3	+0.5
R26127	4	3826.5	R 26126*		

Table IV contd.

Ferguson ν_{vac} in cm^{-1}	I	Present Experiments λ_{air} A.U.	Present Experiments ν_{vac} in cm^{-1}	Assignment v' , v"	O - C in cm^{-1}
	2	3819.7	Q 26173		
R26185.2	4	3817.9	R 26185	1 , 2	-0.3
	3	3811.6	Q 26228		
R26244.3	4	3809.3	R 26244	0 , 1	+0.3
	2	3798.2	Q 26321		
R26329.5	4	3797.0	R 26329	4 , 4	0
	1	3787.5	Q 26395		
R26405.2	2	3786.1	R 26405	3 , 3	+0.4
	1	3777.9	Q 26462		
R26475.3	3	3776.0	R 26476	2 , 2	+0.2
R26537.8	4	3769.2	Q 26523		
	4	3767.2	R 26537	1 , 1	-0.6
	4	3761.1	Q 26580		
R26597.9	5	3758.6	R 26599	0 , 0	0
	0	3748.9	Q 26667		
R26676	1	3747.6	R 26676	4 , 3	-1.3
	0	3738.4	Q 26742		
R26754	1	3736.7	R 26754	3 , 2	-0.9
	0	3728.7	Q 26811		
R26825	1	3726.8	R 26825	2 , 1	-1.1
	0	3719.9	Q 26875		
			R	1 , 0	-0.9

* These bands can be arranged as R heads of the main $SnCl^{35}$ ban and also as $SnCl^{37}$ bands.

† These bands measured as R heads of $SnCl^{35}$ bands by Ferguson identified as $SnCl^{37}$ bands in the present analysis.

TABLE V

Experimental data and the assignment of $SnCl^{35}$ band heads in the region 3650-3450A.

Ferguson ν_{vac} in cm^{-1}	I	Present Experiments λ_{air} in A.U.	Present Experiments ν_{vac} in cm^{-1}	Assignment v', v"	O - C in cm^{-1}
	0	3651.0	Q 27382	(4 , 7)	+1.0
	0	3650.7	R 27384		
	1	3641.9	Q 27450	3 , 6	-0.4
	0	3641.6	R 27453		
	1	3633.7	Q 27512	2 , 5	-0.4
	0	3633.1	R 27517		
	2	3626.2	Q 27569	1 , 4	+0.4
	0	3625.6	R 27574		
	3	3606.9	Q 27717	(4 , 6)	-1.0
	1	3604.0	R 27739		
	3	3597.5	Q 27789	3 , 5	+0.6
			R		
	4	3589.1	Q 27854	2 , 4	+0.2
	2	3588.7	R 27857		
	2	3581.6	Q 27913	1 , 3	0
	0	3581.0	R 27917		
	2	3574.6	Q 27967	0 , 2	+1
	0	3574.2	R 27970		
Q 28056	1	3563.2	Q 28057	4 , 5	-0.2
	0	3562.8	R 28060		
Q 28131.9	2	3553.7	Q 28132	3 , 4	+1.0
	1	2553.3	R 28135		
Q 28198.8	2	3545.2	Q 28199	2 , 3	+1.2
	1	3544.6	R 28204		
Q 28315.7	3	3530.7	Q 28315	0 , 1	-0.2
			R		
Q 28397.	1	3520.4	Q 28398	4 , 4	-1.8
	0	3520.0	R 28401		

Table V contd.

Fergusons ν_{vac} in cm^{-1}	I	Present Experiments λ_{air} in A.U.	Present Experiments ν_{vac} in cm^{-1}	Assignment v' , v"	O - C in cm^{-1}
Q 28473.5	2	3511.0	Q 28474	3 , 3	+0.6
28478.8	0	3510.4	R 28479		
Q 28544.5	3	3502.4	Q 28544	2 , 2	-0.4
R 28551	2	3501.5	R 28551		
Q 28607.5	4	3494.5	Q 28608	1 , 1	-0.4
R 28615.7	3	3493.7	R 28615		
Q 28665.3	5	3487.4	Q 28666	0 , 0	0
R 28676.1	4	3486.2	R 28676		
Q 28741.	0	3478.2	Q 28742 R	4 , 3	-1.4
	1	3468.9	Q 28819	3 , 2	+1.4
	0	3463.3	R 28824		
	1	3460.0	Q 28893 R	2 , 1	+0.6
	1	3452.1	Q 28960 R	1 , 0	+1.2

TABLE VI

DESLANDRE'S SCHEME OF THE BAND SYSTEM 3950-3720A OF Sncl.

v'' / v'	0	1	2	3	4	5	6	ΔG'(v+½) Obs.	ΔG'(v+½) Cal.
0	26580	352 26228	350 25878	349 25529					
		295	295	295	297			295·5	295·9
1	26875	352 26523	350 26173	347 25826	346 25480				
		288	289	288	288			288·3	288·5
2		26811	349 26462	348 26114	346 25768	345 25423			
			280	281	282	283		281·5	281·1
3			26742	347 26395	345 26050	344 25706	343 25363		
				272	271	271	273	271·7	273·7
4				26667	346 26321	344 25977	341 25636		
		352	349·7	347·8	345·8	344·3	342	←	ΔG''(v+½) Obs.
		352·3	350·3	348·3	346·3	344·3	342·3	←	ΔG''(v+½) Cal.

TABLE VII

DESLANDRES SCHEME OF THE BAND SYSTEM 3650-3450 A OF SnCl.

v'' / v'	0	1	2	3	4	5	6	7	ΔG'(v+½) Obs.	ΔG'(v+½) Cal
0	28666	351 28315	348 27967						293·3	292·8
	294	293	293							
1	28960	352 28608	348 28260	347 27913	345 27569				285	284·8
		285	284	286	285					
2		28893	349 28544	345 28199	345 27854	342 27512			276·3	276·8
			275	275	278	277				
3			28819	345 28474	342 28132	343 27789	339 27450		267·3	268·8
				268	266	268	267			
4				28742	344 28398	341 28057	340 27717	335 27382		
		351·5	348·3	345·7	344	342	339·5	335	←	ΔG''(v+½) Obs.
		351·2	348·8	346·4	344	341·6	339·2	336·8	←	ΔG''(v+½) Cal.

than ± 1.0 cm^{-1}. It can be seen from this table that a large number of new bands have been obtained in the present experiments. The Deslandéres schemes for both the groups of bands are shown in tables VI and VII.

All the bands observed could be represented fairly well by the formulae

3800 group : $\nu = 26580 + 299.6v' - 3.7v'^2 - 353.3v'' + 1.0v''^2$

3500 group $\nu = 28666 + 296.8v' - 4.0v'^2 - 352.4v'' + 1.2v''^2$

The vibrational constants derived from the present analysis are slightly different from those obtained by Ferguson the difference being appreciable in the case of 3800A group. The appreciable difference in the case of the 3800A group is probably because the vibrational constants derived by Ferguson were from the data which include many calculated values of the Q heads instead of the direct experimental values.

The calculated and observed isotopic displacements are recorded in tables VIII and IX. The close agreement between these values shows the correctness of the vibrational analysis. The doublet nature of the ground and upper states suggests as was supposed by earlier workers that the emitter is very likely the SnCl molecule and the transition is probably $^2\Delta \rightarrow {}^2\pi$,the doublet separations of $^2\Delta$ and $^2\pi$ being 273.9 cm^{-1} and 2360 cm^{-1} respectively.

TABLE VIII

Isotopic displacements of the bands in the region 3950-3700A

(3800 group)

(Q Heads)

Ferguson ν' $SnCl^{37}$	Present Experiments ν' $SnCl^{37}$	Present Experiments ν $SnCl^{35}$	Assignment v' , v"	$(\nu'-\nu)$ Obs.	$(\nu'-\nu)$ Cal
	25549	25529	0 , 3	20	22.2
	25658	25636	4 , 6	22	21.4
	25721	25706	3 , 5	15	18.4
	25785	25768	2 , 4	17	17.7
	25841	25826	1 , 3	15	16.3
	25893	25878	0 , 2	15	15.1
25996	25991	25977	4 , 5	14	14.4
26064.2	26061	26050	3, , 4	11	12.4
26130.7	26126	26114	2 , 3	12	10.6
	26182	26173	1 , 2	9	9.2
26237.9	26236	26228	0 , 1	8	7.9
26329	26329	26321	4 , 4	8	7.5
26400	26401	26395	3 , 3	6	5.3

TABLE IX

Isotopic displacements of the bands in the region 3650-3450A

(3500A group)

(Q Heads)

Ferguson $\nu' SnCl^{37}$	Present Experiments $\nu' SnCl^{37}$	Present Experiments $\nu SnCl^{35}$	Assignment v' , v"	$(\nu'-\nu)$ Obs.	$(\nu'-\nu)$ Calc
	27478	27450	3 , 6	28	26.9
	27436	27512	2 , 5	24	25
	27594	27569	1 , 4	25	23.4
	27808	27789	3 , 5	19	20
	27874	27854	2 , 4	20	18
	27928	27913	1 , 3	15	16.4
	27983	27967	0 , 2	16	15.1
28070	28072	28057	4 , 5	15	15.4
28143.	28144	28132	3 , 4	12	13.
28209.1	28210	28199	2 , 3	11	11
28269.7	28269	28260	1 , 2	9	9.3
28322.8	28322	28315	0 , 1	7	7.8
28403	28405	28398	4 , 4	7	8.4
	28479	28474	3 , 3	5	6.
	28548	28544	2 , 2	4	3.9
	28610	28608	1 , 1	2	2.1
	28743	28742	4 , 3	1	1
	28890	28893	2 , 1	-3	-3.3
	28956	28960	1 , 0	-4	-5.7

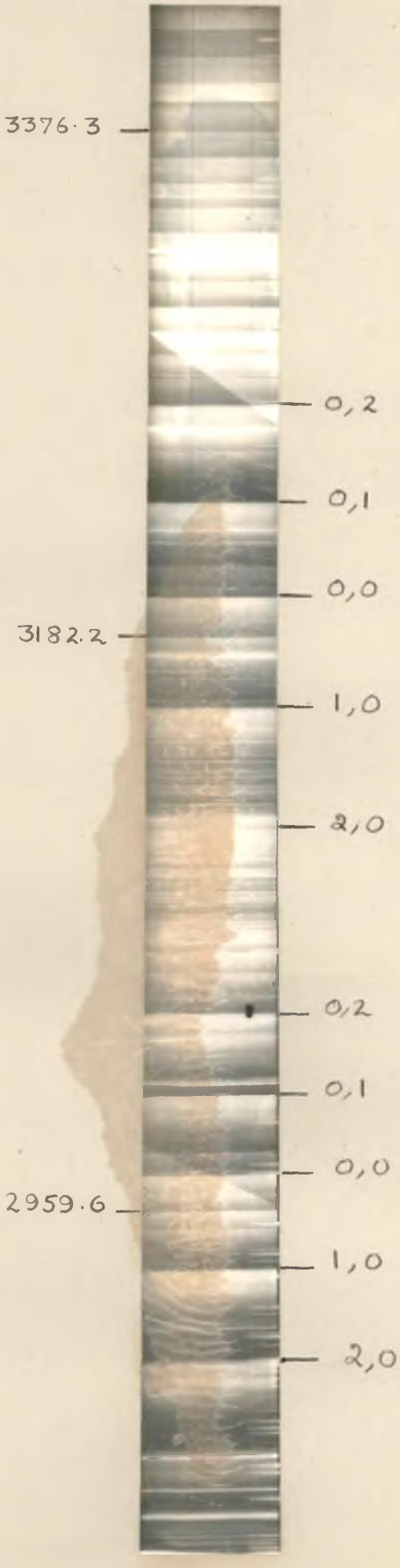

Fig. 5. The enlargement of 3400-2800A system of SnCl taken on the first order grating.

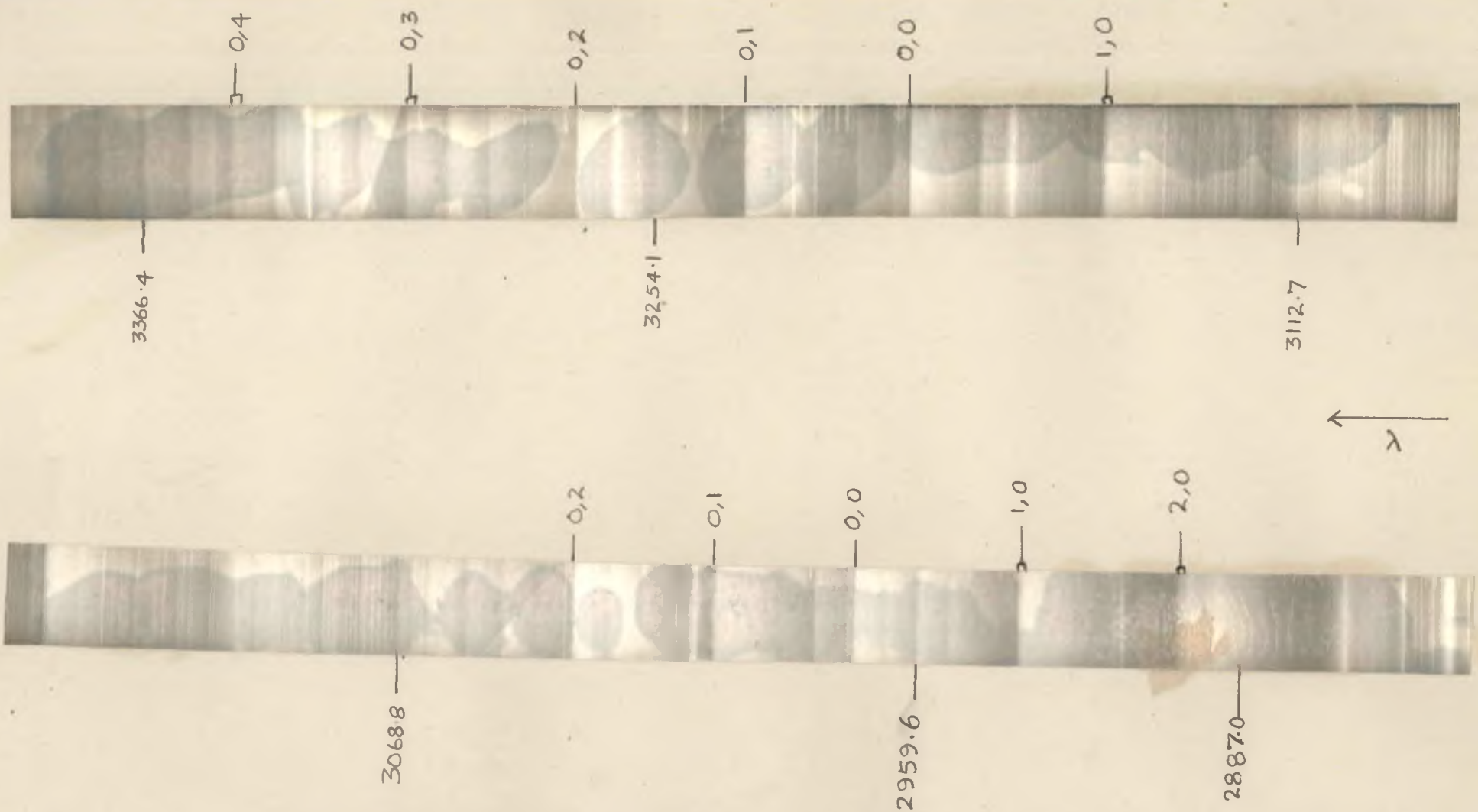

Fig. 6. The enlargement of 3400-2800A system of SnCl taken on the second order grating Spectrograph
a. 3400-3015A (α group)
b. 3015-2800A (β group)

SECTION C

The band system in the region 3400-2800A.

Jevons[1] recorded this band system in the region 3400-2800A, using a grating spectrograph having a dispersion of 7A/m.m. He has stated that he used larger slit widths as the intensity of this band system was very poor. The intensity of this band system has been found to considerably increase in the present experiments when $SnCl_4$ vapour has been excited in the presence of argon. The system has been photographed in the 1st and 2nd orders of the Jerrel Ash 3.4 meter spectrograph. Kodak B_{20} plates were used with the exposure times of 15 minutes and 2 hours in the 1st and 2nd orders respectively. The enlargements of this system are shown in Figs.5 and 6. It has been found that all the bands in this system showed P and Q heads. Jevons did not observe these double heads probably because of the large width of the slit he had to use to photograph the spectrum. A large number of bands which were marked by Jevons as doubtful are now obtained with good intensity. Also the bands that were masked by nitrogen second positive on Jevons[1] plates could now be measured as the nitrogen was completely absent in the present experiments. The wavelength data of P and Q heads of $SnCl^{35}$ bands measured from the plates taken on the 2nd order of the grating spectrograph are given in tables X & XI in which Jevons data are also included for comparison. The vibrational schemes are shown in tables XII and XIII.

TABLE X

Experimental data and the assignment of $Sncl^{35}$ band heads in the region 3405-3070.

Jevons ν_{vac} cm^{-1}	I	Present Experiments λ_{air} A. U.	ν_{vac} cm^{-1}	Assignment v' , v"	O - C in cm^{-1}
			P		
29358	1	3405.1	Q 29359	2 , 8	-0.4
	0	3386.6	P 29519		
29520	1	3386.3	Q 29522	0 , 5	-0.5
	0	3376.6	P 29607		
29612	2	3376.3	Q 29610	1 , 6	-0.3
	2	3366.4	P 29697		
	4	3366.2	Q 29699	2 , 7	+1.3
	1	3356.8	P 29782		
29781	3	3356.6	Q 29784	3 , 8	-0.7
	2	3347.5	P 29864		
29865	4	3347.2	Q 29867	0 , 4	+0.2
	3	3338.1	P 29948		
29951	4	3337.8	Q 29951	1 , 5	-0.6
	2	3328.6	P 30034		
30035	4	3328.2	Q 30038	2 , 6	0
			P		
30121	3	3318.9	Q 30122	3 , 7	-1.0
	4	3300.0	P 30294		
30294	5	3299.6	Q 30298	1 , 4	+1.1
	2	3291.0	P 30377		
30379	4	3290.5	Q 30380	2 , 5	+0.7
			P		
	3	3281.6	Q 30464	3 , 6	
	5	3271.5	P 30558		
30778	6	3271.1	Q 30562	0 , 2	+0.6
			P		
30641	4	3262.3	Q 30644	1 , 3	+0.8
	2	3254.1	P 30721		
30721	4	3253.7	Q 30725	2 , 4	+0.4

Table X contd.

Jevons ν_{vac} cm^{-1}	I	Present Experiments λ_{air} A.U.	Present Experiments ν_{vac} cm^{-1}	Assignment v' , v"	O - C in cm^{-1}
30809	0	3245.3	P Q 30805	3 , 5	+0.4
30909	6 8	3234.3 3234.1	P 30908 Q 30912	0 , 1	+0.3
30989	4	3225.8	P Q 30991	1 , 2	-0.5
31147	2 3	3208.8 3209.6	P 31146 Q 31148	3 , 4	-1.9
31226	0	3201.4	P Q 31227	4 , 5	-0.5
31262	8 10	3197.9 3197.6	P 31262 Q 31264	0 , 0	0
31339	6 8	3190.0 3189.8	P 31339 Q 31341	1 , 1	-0.8
31416	4 5	3182.2 3181.9	P 31416 Q 31419	2 , 2	-0.2
	2	3174.1	P Q 31496	3 , 3	+0.3
31569	2	3166.4	P Q 31573	4 , 4	+0.2
31692	4 5	3154.7 3154.3	P 31690 Q 31694	1 , 1	-0.1
31766	2	3146.8	P Q 31769	2 , 1	-0.5
	0	3132.	P Q 31919	4 , 3	-0.1
32120	3 4	3112.7 3112.3	P 32117 Q 32121	2 , 0	-0.8
32195	2	3105.3	P Q 32194	3 , 1	0.8
32267	1 2	3098.3 3098.5	P 32264 Q 32266	4 , 2	-1.4
32547	2	3071.7	P Q 32546	3 , 0	-1.1

TABLE XI

Experimental data and the assignment of $SnCl^{35}$ band heads in the region 3135-2800A.

Jevons ν_{vac} in cm^{-1}	I	Present Experiments λ_{air} in A.U.	Present Experiments ν_{vac} in cm^{-1}	Assignment v', v"	O-C in cm^{-1}
31988	1	3135.4	Q 31985 P	1 , 6	+1.1
32080	1 2	3116.5 3116.7	P 32078 Q 32076	2 , 7	-1.2
32235	1 2	3101.6 3101.3	P 32232 Q 32235	0 , 4	-0.4
32328	2 2	3093.0 3092.8	P 32322 Q 32324	1 , 5	+0.9
32414	2 2	3084.5 3084.4	P 32410 Q 32412	2 , 6	+0.4
32502		3076.1 3075.9	P 32499 Q 32501	3 , 7	+0.9
32582		3068.8 3068.6	P 32577 Q 32579	0 , 3	-0.2
32670	3 4	3060.7 3060.5	P 32663 Q 32665	1 , 4	+0.4
32756	3 3	3052.7 3052.5	P 32748 Q 32751	2 , 5	+0.2
32844	1 1	3044.5 3044.2	P 32837 Q 32840	3 , 6	+1.1
32924	6 7	3036.6 3036.4	P 32922 Q 32924	0 , 2	-1
33008	3 5	3028.7 3028.5	P 33008 Q 33010 P	1 , 3	+0.7
33092	1	3020.9	Q 33093	2 , 4	-0.4
33274	3 7	3004.8 3004.6	P 33270 Q 33273	0 , 1	-0.8

Table XI contd.

Jevons $\bar{\nu}_{vac}$ in cm^{-1}	I	Present Experiments λ_{air} in A.U.	Present Experiments $\bar{\nu}_{vac}$ in cm^{-1}	Assignment v' , v"	O-C in cm^{-1}
33356	4	2997.2	P Q 33355	1 , 2	-0.1
33435	2	2980.9	P Q 33437	2 , 3	0
33521	2	2982.4	P Q 33520	3 , 4	+1.3
33600	0 1	2975.5 2975.3	P 33598 Q 33600	4 , 5	+1
33622	6 0	2973.4 2973.1	P 33622 Q 33625	0 , 0	0
33702	4 5	2966.3 2966.1	P 33702 Q 33704	1 , 1	+0.1
33779	5	2959.6	P Q 33782	2 , 2	-0.8
33860	7	2959.3	P Q 33862	3 , 3	-0.3
34109	0	2938.7	P Q 34019	5 , 5	-0.5
34052	4 6	2935.9 2935.6	P 34051 Q 34055	1 , 0	-0.1
34130	3	2929.0	P Q 34131	2 , 1	-0.6
	0	2922.7	P 34205		
	1	2922.5	Q 34207	3 , 2	-1.1
34285	0 1	2916.2 2915.8	P 34281 Q 34286	4 , 3	+0.8
	0 0	2909.5 2909.3	P 34360 Q 34362	5 , 4	-0.1
34480	3 5	2899.5 2899.3	P 34479 Q 34481	2 , 0	-1.8

Table XI contd.

Jevons ν_{vac} in cm^{-1}	I	Present Experiments λ_{air} in A.U.	Present Experiments ν_{vac} in cm^{-1}	Assignment v' , v"	O-C in cm^{-1}
34556	2 4	2893.1 2892.9	P 34555 Q 34557	3 , 1	-0.1
34628	2 3	2887.0 2886.8	P 34628 Q 34630	4 , 2	-1.0
	1	2880.3	P Q 34708	5 , 3	+2.3
	0	2858.0	P Q 34979	4 , 1	-0.8
	0	2829.6	P Q 35330	4 , 0	-1.0
	0	2824.0	P Q 35400	5 , 1	-0.3

TABLE XII

THE VIBRATIONAL SCHEME OF THE BAND SYSTEM 3400-3070 A

v' \ v''	0	1	2	3	4	5	6	7	8	ΔG'(v+½) Obs.	ΔG'(v+½) Cal.
0		352	350	348	347	345					
	31264	30912	30562	30214	29867	29522					
		430	429	429	430	431	429			429·7	430·1
1		353	350	347	346	347	341				
	31694	31341	30991	30644	30298	29951	29610				
		427	428	428	427	429	428			427·8	427·7
2		352	350			345	342	339	340		
	32121	31769	31419		30725	30380	30038	29699	29359		
		425	425		423	425	426	423	425	424·6	425·3
3		352			348	343	341	342	338		
	32546	32194		31496	31148	30805	30464	30122	29784		
				423	425	422				423·3	422·9
4				347	346	346					
			32266	31919	31573	31227					
5											
		352·2	350	347·3	347	345·2	341·3	340·5	339	←	ΔG''(v+½) Obs.
		352·3	350·3	348·3	346·3	344·3	342·3	340·3	338·9	←	ΔG''(v+½) Cal

TABLE XIII

THE VIBRATIONAL SCHEME OF THE BAND SYSTEM 3135-2820A

v'' / v'	0	1	2	3	4	5	6	7	ΔG'(v'+½) Obs.	ΔG'(v'+½) Cal.
0	33625	352 33273	349 32924	345 32579	344 32235					
	430	431	431	431	430				430·6	430·1
1	34055	351 33704	349 33355	345 33010	345 32665	341 32324	339 31985			
	426	427	427	427	428	427	427		427	427·7
2	34481	350 34131	349 33782	345 33437	344 33093	342 32751	339 32412	336 32076		
		426	425	425	427		428	425	426	425·3
3		350 34557	345 34207	342 33862	33520		32840	339 32501		
		422	423	424					423	422·9
4	35330	351 34979	349 34630	344 34286		33600				
		421		422		419			4207	420·5
5		35400		346 34708	343 34362	34019				
		351	349·2	344·8	344·2	342	339	337·5	←	ΔG''(v'+½) Obs.
		351·2	348·8	346·4	344	341·6	339·2	336·8	←	ΔG''(v'+½) Cal.

TABLE XIV

Isotopic displacements for 3405-3070A group.

Jevons $SnCl^{37}$ ν'	Present Experiments $SnCl^{35}$ ν_{vac} in cm^{-1}	v', v"	$SnCl^{37}$ ν'_{vac} in cm^{-1}	$(\nu'-\nu)$Obs	$(\nu'-\nu)$Cal.
	29610	(1 , 6)	29643	33	33.7
	29699	(2 , 7)	29732	33	32.7
	29867	(0 , 4)	29897	30	28.2
	29951	(1 , 5)	29977	26	25.8
	30038	(2 , 6)	30062	24	25.4
	30122	(3 , 7)	30147	25	24.1
	30214	(0 , 3)	30234	20	21.1
	30298	(1 , 4)	30317	19	19.8
	30380	(2 , 5)	30396	16	17.5
	30725	(2 , 4)	30736	11	11.6
	30805	(3 , 5)	30815	10	9.3
	31148	(3 , 4)	31151	3	3.3
31416	31419	(2 , 2)	31416	-3	-2.7
31684	31694	(1 , 0)	31686	-8	-6
32013	32121	(2 , 0)	32103	-18	-17.2
32171	32194	(3 , 1)	32175	-19	-18.1
32520	--	3 , 0			

TABLE XV

Isotopic displacements in 3135-2800A group.

Q heads

Jevons	Present Experiments		Assignment		
$SnCl^{37}$ head ν'	$SnCl^{35}$ head ν	$SnCl^{37}$ head ν'	v' , v"	$(\nu'-\nu)$ Obs.	$(\nu'-\nu)$ Cal.
	31985	32017	(1 , 6)	32	33.6
	32076	32107	(2 , 7)	31	32.1
	32235	32261	(0 , 4)	26	28.1
	32324	32350	(1 , 5)	26	26.7
	32412	32436	(2 , 6)	24	25.3
	32501	32523	(3 , 7)	22	23.9
	32579	32599	(0 , 3)	20	21.1
	32665	32685	(1 , 4)	20	19.8
	32751	32769	(2 , 5)	18	18.4
	32840	32856	(3 , 6)	16	17.1
	33010	33025	(1 , 3)	14	12.7
	33520	33523	(3 , 4)	3	3.3
33799	33782	33779	(2 , 2)	-3	-2.7
34042	34055	34046	(1 , 0)	-9	-9.9
	34131	34120	(2 , 1)	-11	-9.9
34464	34481	34464	(2 , 0)	-17	-17.2
34532	34557	34539	(3 , 1)	-18	-18.1
34884	-		(3 , 0)		

The bands could be represented well within the experimental errors of ± 1.0 or ± 1.5 cm^{-1} by the formulae

group α ; $\nu = 31264 + 431.3v' - 1.2v'^2 - 353.3v'' + 1.0v''^2$

group β ; $\nu = 33625 + 431.3v' - 1.2v'^2 - 352.4v'' + 1.2v''^2$

The vibrational constants of the lower state of this system are the same as those of the lower state of the 4000-3400A system. The transition involved as suggested by Jevons, is probably $^2\Sigma \longrightarrow {}^2\Pi$

The observed and calculated isotopic shifts are listed in tables XIV & XV (~~14 & 15~~). It can be seen from these tables that 30 isotopic components were found in the present experiments against 6 components reported earlier. The agreement between observed and calculated shifts supports the validity of the vibrational analysis.

The present work on the two band systems 4000-3400A and 3400-2800A has not only given probably better vibrational constants for the upper states, but also made it possible to obtain correct vibrational constants for the common lower state of these two systems.

The occurance of the two band-systems 4000-3350A and 3400-2800A in absorption, as observed by Fowler, suggests that the common lower state of these two systems is also the ground state of the molecule.

SECTION D

The absorption band system in the region 2450-2250A obtained by Fowler.

The data obtained by Fowler[4] for the 2450-2250A system are listed in table XVI. These bands could be well represented by the formulae

$$\nu = 43656.1 + 392.8v' - 1.40v'^2 - 352.4v'' + 1.2v''^2$$

$$\nu = 41383.8 + 392.8v' - 1.40v'^2 - 353.3v'' + 1.0v''^2$$

The vibrational constants of the lower state are the same as those obtained in sections B and C for the lower state of the two band systems in emission. These differ only slightly from those given by Fowler. The constants of the upper state are the same as those given by him. This band system, as suggested by Fowler, is probably due to a transition from the $^2\pi$ ground state of the molecule to an upper $^2\pi$ state, the doublet separation for which is 67.9 $cm.^{-1}$

TABLE XVI

ν_{vac} in cm^{-1}	I	v' , v"	Obs-Cal calculated from Fowlers constants	Obs-Cal calculated from the constants derived in Sections B & C.
42976.1	2	(0 , 3)i	-1.8	-0.2
43019.7	3	(1 , 3)i	-1.8	+1.2
43325.1	5	(0 , 1)i	+1	+0.4
41032.	0	(0 , 1)ii	-0.8	-1.3
43675.9	8	(0 , 0)i		
41383.8	10	(0 , 0)ii		
44066.	10	(1 , 0)i	-1.3	
41774.4	1	(1 , 0)ii	-0.8	
44453.1	8	(2 , 0)i	-2.8	

i The system corresponding to $^2\Pi_{1/2} \longrightarrow {}^2\Pi_{1/2}$

ii The system corresponding to $^2\Pi_{3/2} \longrightarrow {}^2\Pi_{3/2}$

References

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2. W.F.C. Ferguson: Physic. Rev. 32, 607, 1928.
3. R.K. Asundi, S.M. Karim and R. Samuel; Proc. Phy. Soc. (London)50,581,1938.
4. C.A. Fowler Jr., Physic Rev. 62, 141, 1942.

CHAPTER II

Emission Spectrum of Tin Monobromide.

ABSTRACT

A new band system in the region 6400-5100A has been obtained by exciting the stannic bromide vapour in the presence of argon with an uncondensed transformer discharge. The spectrum was photographed on the first order of the 3.4 meter grating spectrograph. Isotopic shifts due to tin and bromine were observed for some of the bands. The vibrational constants derived from the analysis of this system are

$\omega_e' = 164.1\ cm^{-1}$ $\omega_e'' = 247.08\ cm^{-1}$

$\omega_e' x_e' = 0.9\ cm^{-1}$ $\omega_e'' x_e'' = 0.48 cm^{-1}$

INTRODUCTION

The emission spectrum of SnBr was first observed by Howell and Rochester[1] by exciting the stannic bromide vapour with a high frequency discharge. The observed spectrum consisted of (1) a strong continuum in the region 6500-4400A, (2) a set of diffuse bands in the region 4400-3750A and (3) another continuum with its intensity maximum at 3600A. They also observed another set of diffuse bands which were thought to be due to chloride impurity as some of these bands were similar to the SnCl bands of 2940A system. Jevons[2] later photographed the emission spectrum of SnBr on a high dispersion spectrograph by exciting the stannic bromide vapour in a heavy current discharge. He reported two discrete band systems in the regions 4255-3709A and 3428-3020A and a continuum with the intensity maximum at 2914A, which were not reported earlier by Howell and Rochester. The diffuse bands reported by Howell and Rochester were not observed by Jevons. The discrete band system in the region 3428-3020A was analysed by Jevons as due to $a^2\Sigma \rightarrow {}^2\pi$ transition and the other band system in the region 4255-3709A was classified as due to a ${}^2\Delta \rightarrow {}^2\pi$ transition. The electronic doublet separation of the common ${}^2\pi$ lower state is 2467 cm^{-1} and that of the ${}^2\Delta$ state is 371 cm^{-1}.

Stannic chloride vapour when excited in the presence of argon gives a discrete band system in the

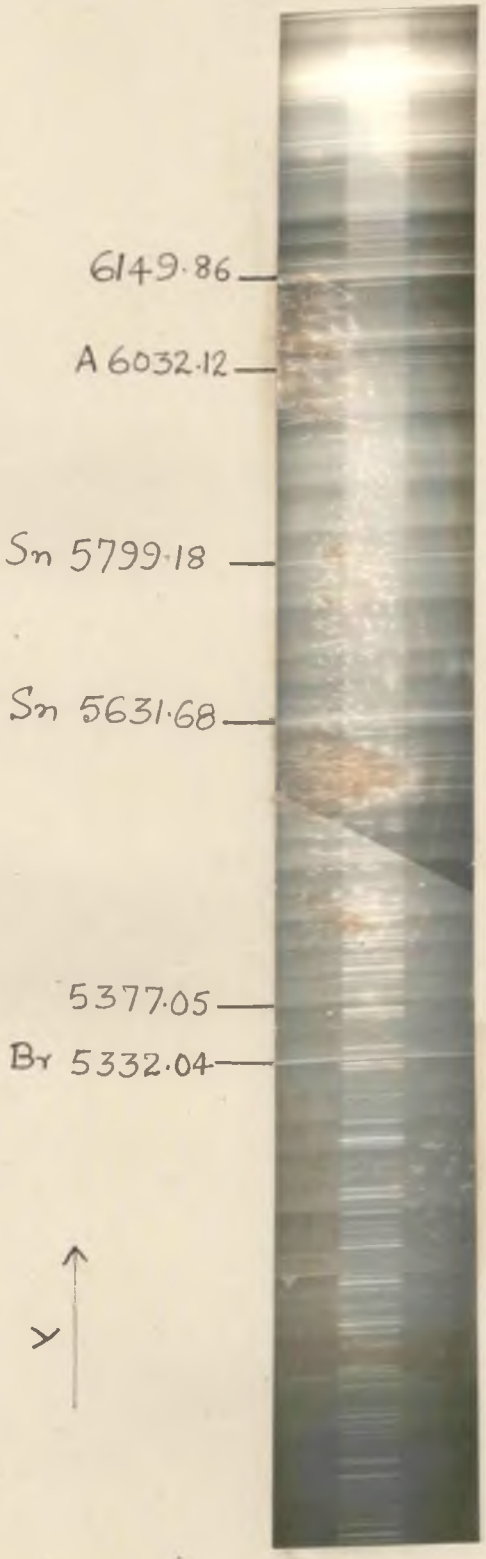

Fig. 1. The enlargement of 6400–5100A system of Sulphur taken on Hilger Spectrograph.

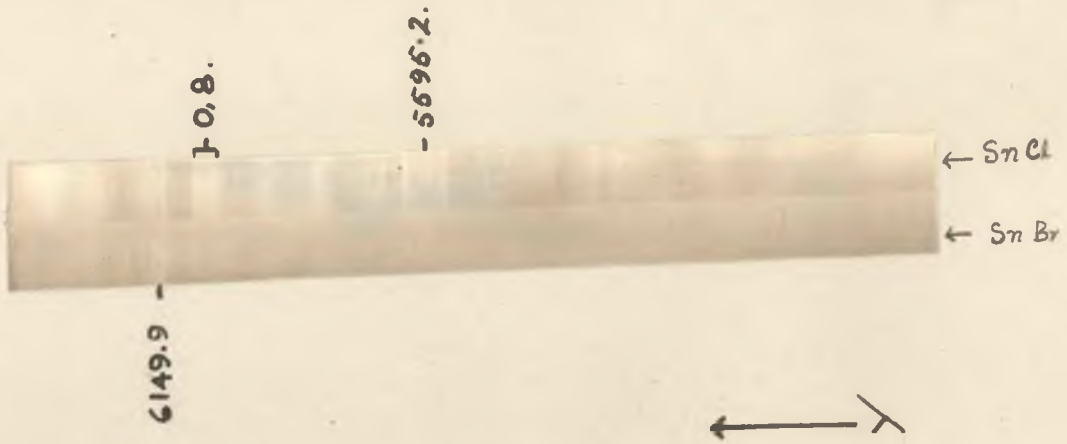

Fig. 2. The enlargement of the juxtaopposed spectra of SnCl and SnBr in the visible region.

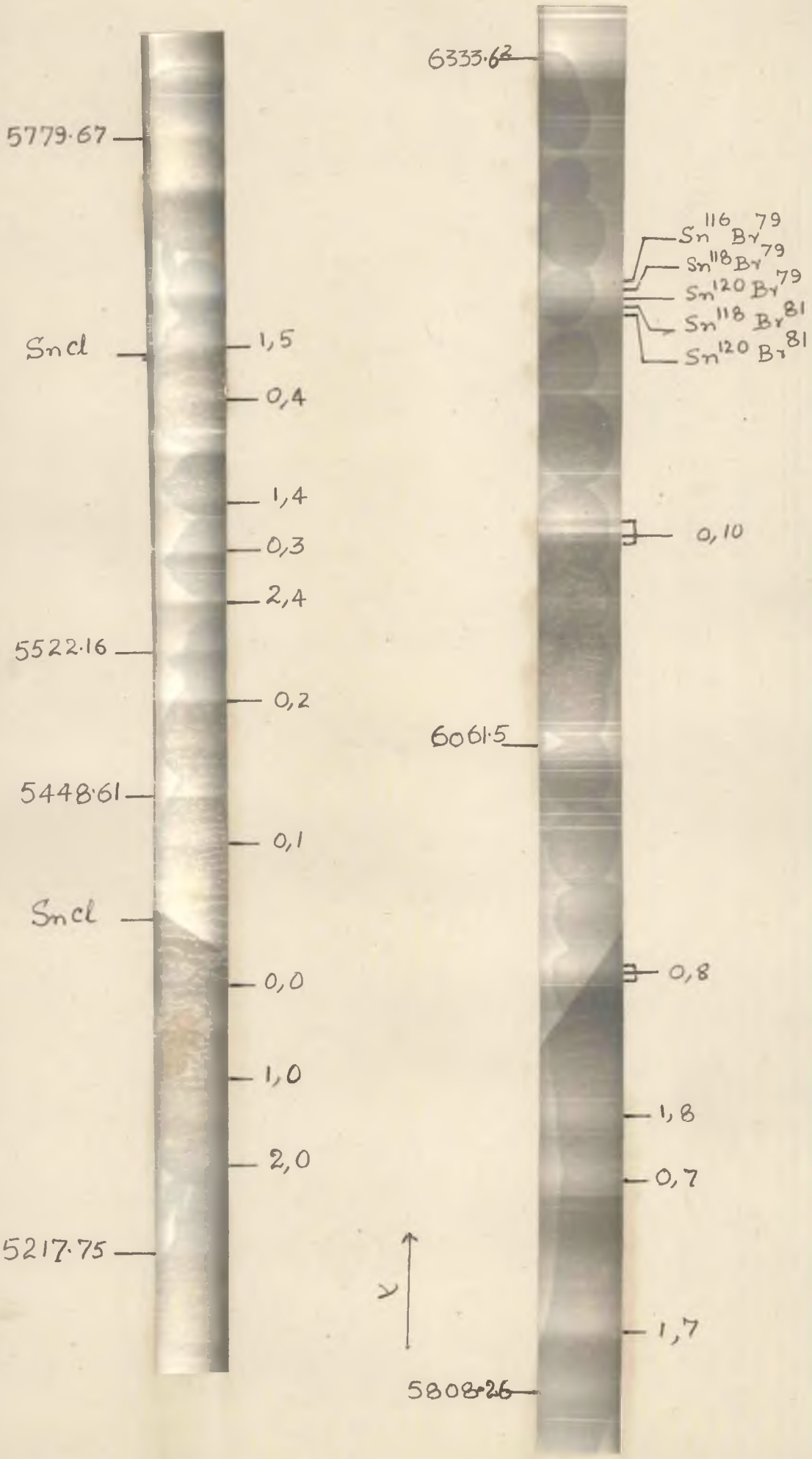

Fig. 3. The enlargement of H 6400-5100A region of Sulphur taken on the first order grating Spectrograph.

region where only continuum appears when it is excited without the presence of argon. The spectrum of SnBr, as discribed earlier, consists of continua similar to that of SnCl spectrum when $SnBr_4$ is excited without the presence of argon. It was expected that SnBr when excited in the presence of argon might show up a new band system analogous to that of SnCl discussed in Chapter I. Experiments were therefore carried out in this direction and the results obtained are given in this chapter.

Experimental Results

Stannic bromide vapour was excited in the presence of argon with an uncondensed transformer discharge. The experimental details are similar to those described earlier in the case of SnCl. As the pressure of the argon is increased, the continuum in the region 6500-4400A goes down in intensity and a new discrete band system in the region 6400-5100A results. It may be mentioned here that the continuum in the region 6500-4400A will not disappear completely but persists in the region 5200-4400A. Some of the bands of the new system are overlapped by this continuum. The two discrete band systems reported by Jevons also do persist along with the continua whose intensity maxima are at 3600A and 2913A.

The band system was first photographed on the

TABLE I

Wavelength Data for SnBr.

I	Wavelength λ_{air} A.U.	Assignment v' , v"	Wavenumber ν_{vac} in cm^{-1}	O - C in cm^{-1}
4	6333.62	0 , 12	15785	+0.6
4	6240.64	0 , 11	16020	-0.4
5	6149.86	0 , 10	16256	-0.8
5	6061.5	0 , 9	16493.5	-0.7
2	6001.87	1 , 9	16656.8	-0.8
3	5974.9	0 , 8	16732.1	-0.8
4	5917.25	1 , 8	16895.0	-1.2
3	5890.21	0 , 7	16972.6	+0.2
3	5834.32	1 , 7	17135.2	-0.4
1	5808.26	0 , 6	17212.1	-0.7
2	5779.67	2 , 7	17297.2	+0.2
3	5753.74	1 , 6	17375.2	-0.3
3	5727.4	0 , 5	17455.1	+0.8
1	5700.23	2 , 6	17538.3	+0.8
4	5674.4	1 , 5	17618.1	+0.6
2	5648.92	0 , 4	17697.6	+0.9
10	5622.79	2 , 5	17779.8	+0.9
4	5597.52	1 , 4	17860.1	+0.2
8	5572.28	0 , 3	17941.1	+0.9
5	5547.17	2 , 4	18022.2	+0.9
2	5522.16	1 , 3	18104	+0.8
5	5497.27	0 , 2	18185.8	+1.4

Table I contd.

I	Wavelength λ_{air} A.U.	Assignment v' , v"	Wavenumber ν_{vac} in cm^{-1}	O - C in cm^{-1}
2	5473.4	2 , 3	18265.1	+0.5
4	5448.61	1 , 2	18348.2	+0.5
2	5424.37	0 , 1	18430.2	+0.6
3	5401.04	2 , 2	18509.8	+0.9
5	5377.05	1 , 1	18592.4	-0.4
3	5353.03	0 , 0	18675.8	0
5	5330.66	2 , 1	18754.2	0
3	5306.91	1 , 0	18838.1	-0.9
2	5285.84	3 , 1	18913.2	-0.4
1	5261.69	2 , 0	19000	-0.4
0	5241.81	4 , 1	19072	+0.6
2	5217.75	3 , 0	19160	+0.2
1	5175.32	4 , 0	19317.1	-0.5

TABLE II

THE VIBRATIONAL SCHEME OF THE BAND SYSTEM 6900-5100 A OF SnBr.

v'' / v'	0	1	2	3	4	5	6	7	8	9	10	11	12	$\Delta G'(v+1/2)$ Obs.	$\Delta G'(v+1/2)$ Cal.
		245·6	244·4	244·7	243·5	242·5	243·0	239·5	240·5	238·6	237·5	236	235		
0	18675·8	18430·2	18185·8	17941·1	17697·6	17955·1	17212·1	16972·6	16732·1	16493·5	16256	16020	15785		
	162·3	162·2	162·4	162·9	162·5	163	163·1	162·6	163·2	163·3				162·8	163·2
		245·7	244·2	244·2	243·9	242·0	242·9	240·0	239·9	238·5					
1	18838·1	18592·4	18348·2	18104	17840·1	17618·1	17375·2	17135·2	16895·3	16656·8					
	161·9	161·8	161·6	161·1	162·1	161·7	163·1	162						161·9	161·4
		245·8	244·4	244·7	242·9	242·4	241·5	241·1							
2	19000	18754·2	18509·8	18265·1	18022·2	17779·8	17538·3	17297·2							
	160	159												159·5	159·6
		246·8													
3	19160	18913·2													
	157·1	158·8												158	157·8
		245·1													
4	19317·1	19072													
		245·8	244·3	244·5	243·4	242·3	242·5	240·2	239·7	238·6	237·5	236	235	←	$\Delta G''(v+1/2)$ Obs
		246·2	245·2	244·2	243·2	242·2	241·2	240·2	239·2	238·2	237·2	236·2	235·2	←	$\Delta G''(v+1/2)$ Cal.

Carl-zeiss 3-prism glass spectrograph. Fig. 1 shows the enlargement of the spectrum taken on this spectrograph. The band system is very strong and the bands are degraded to lower frequency side.

As the appearence of this band system is very similar to that of the SnCl band system (in the visible region) discussed in section A of the earlier chapter, a juxta-posed spectrum with SnCl was taken on the prism spectrograph whose enlargement is shown in Fig.2 II. It can be seen from this that some of the SnCl intense bands do appear but with much reduced intensity in the spectrum of SnBr, probably because of the chloride impurity in the sample of stannic bromide.

The spectrum was later photographed on the first order of the 3.4 meter grating spectrograph whose dispersion is 5A/m.m. Ilford panchromatic plates were used and only 10 minutes exposure was found to be sufficient to record the spectrum. The enlargement of this system is shown in Fig.3 III. SnCl bands appearing as due to chloride impurity are marked as such in Fig.3 III. The wavelengths and wavenumbers measured from the plates taken on the grating spectrograph are recorded in table I. The error in the measurements might be $\pm 1 cm^{-1}$. Deslanders scheme is shown in table II. The bands observed could be fairly well represented by the equation.

$$\nu = 18675 + 163.3\,v' - 0.9v'^2 - 246.6\,v'' + 0.48v''^2$$

This band system is analogous to the new band system of SnCl discussed in Chapter I.

Isotopic shift

Tin has ten natural isotopes with the following natural abundance ratio

Sn^{112} = 1.01	Sn^{118} =23.84
Sn^{114} = 0.68	Sn^{119} = 8.68
Sn^{115} = 0.35	Sn^{120} =32.75
Sn^{116} =14.28	Sn^{122} = 4.74
Sn^{117} = 7.67	Sn^{124} = 6.01

Out of these ten isotopes the components due to Sn^{120}, Sn^{118} and Sn^{116} are expected to be favourable for observation.

The two bromine isotopes Br^{79} and Br^{81} have the natural abundance ratio 50.6:49.4. So in the full spectrum of SnBr we should expect six components corresponding to Sn^{120} Br^{81}, Sn^{120} Br^{79}, Sn^{118} Br^{81}, Sn^{118} Br^{79}, Sn^{116} Br^{81} and Sn^{116} Br^{79}. The components due to the last mentioned two isotopic species are expected to be much weaker than the other and they are observed in a very few bands. One can see from Fig.3 that the band heads which are sharp near the origin of the system will gradually become diffuse as one goes to longer wavelengths and finally show the different expected components of the

TABLE III

Isotopic displacements in the 6400-5100 system of SnBr.

v', v"	$^{120}SnBr^{79}$	$^{118}SnBr^{79}$	$^{116}SnBr^{79}$	Isotopic shift due to tin. Obs*	Isotopic shift due to tin. Cal*	$^{120}SnBr^{81}$	$^{118}SnBr^{81}$	$^{116}SnBr^{81}$	Isotopic shift due to bromine Obs**	Isotopic shift due to bromine Cal**
0 , 12	15785	15776	1567	9.3	8.7	15805	15795		19.5	21.9
0 , 11	16020	16012	16004	8	7.8	16039	16031		19	20.1
0 , 10	16256	16249		7.5	7	16274	16266		17.5	18.3
0 , 9	16493.5	16486	16480	7.1	6.3	16510	16502		16.3	16.5
0 , 8	16732.1	16725	17719	6.4	5.6		16742	16736	17	14.7
1 , 8	16895	16890	16885	4.7	5.1		16903	16899	13.5	13.5
2 , 7	17297.2					17307.4			10.2	10.5
1 , 6	17375.2					17384.5			9.3	9.9
0 , 5	17455.1					17465			9.9	9.3
2 , 6	17538.3					17546.8			8.5	8.7
1 , 4	17860					17866			6	6.3
0 , 3	17941					17947			6	5.7
1 , 3	18104					18109			5	4.5
0 , 2	18185.8					18189			3.2	3.9

* Since the isotopic shifts between $Sn^{120}Br^{81,79}$ and $Sn^{116}Br^{81,79}$; $Sn^{118}Br^{81,79}$ and $Sn^{116}Br^{81,79}$ are almost the same their, mean value is given.

** Since the isotopic shifts between $Sn^{120,118,116}Br^{79}$ and $Sn^{120,118,116}Br^{81}$ are almost the same, their mean value is given.

isotopic species well resolved from one another. The observed and calculated isotopic shifts are listed in table III and the close agreement of these indicates the probable correctness of the vibrational assignment.

References

1. H.G. Howell and G.D. Rochester; Proc. Univ. Durham Phil. Soc. 9, 126, 1934.

2. W. Jevons and L.A. Bashford; Proc. Phy. Soc. (London,) 49, 554, 1937.

CHAPTER III

Emission Spectrum of SiCl

ABSTRACT

A new band system in the region 6200-4700Å has been obtained by exciting the silicon tetrachloride vapour in the presence of argon with an uncondensed transformer discharge. The spectrum was photographed on a carl-zeiss 3-prism glass spectrograph and also on the first order of a 3.4 meter grating spectrograph. The band system is analysed and it is analogous to the new systems of SnCl and SnBr. Further the band system in the region 3200-2850Å reported by earlier workers is photographed in the second order of the grating spectrograph in which a large number of new bands are obtained. The vibrational constants of the new system and the improved vibrational constants of the known systems are

System	ν_0 (cm^{-1})	ω_e' (cm^{-1})	$\omega_e'x_e'$ (cm^{-1})	ω_e'' (cm^{-1})	$\omega_e''x_e''$ (cm^{-1})
6200-4700Å	20900	297.4	1.1	519.4	2.1
3200-2850Å	33978.3				
	34184.5	707.8	4.7	534.4	2.1

INTRODUCTION

In an induction coil discharge through the flowing vapour of $SiCl_4$, Jevons[1] has found discrete bands in the regions 3085-2770A and 2602-2331A and two regions of continuous emission between 6300-5300A and 4800-3100A. But however no analysis was proposed. Datta[2] later photographed the discrete bands in the region 3100-2770A on a Hilger E1 quartz spectrograph by exciting the $SiCl_4$ vapour in an uncondensed transformer discharge and analysed the same as due to a transition from a $^2\Sigma$ upper state to a $^2\pi$ lower state, the Electronic separation being 208.1 cm^{-1}. Jevons[3] again excited the $SiCl_4$ vapour in an uncondensed transformer discharge and photographed the spectrum in the region 3100-2250A on a spectrograph similar to that of which Datta has used. He confirmed Datta's analysis for the band system in the region 3100-2770A and analysed the remaining bands in the region 2600-2200A into two systems having the same $^2\pi$ lower state. He analysed the bands in the region 2600-2350A as due to a transition $^2\Delta \rightarrow {}^2\pi$ and those in the region 2350-2200A as due to $^2\Sigma \rightarrow {}^2\pi$.

There are a few bands in the region 2830-2770A whose appearence is different from that of the bands in the region 3100-2850A. Three of them were included into the 3100-2770A system as (2,0), (2,0) and (3,0) while the

remaining bands were left unanalysed. Garg[4] photographed these bands on a Hilger medium quarts spectrograph and analysed all the bands in the region 2830-2770A as belonging to a separate system due to a transition $^2\Sigma \rightarrow {}^2\pi$. The $^2\Sigma$ upper state of the band system in the region 2830-2770A is thus taken to be different from the $^2\Sigma$ upper state of the bands in the region 3100-2830A.

The object of the present investigation is to excite $SiCl_4$ vapour in the presence of argon so as to find out a band system analogous to the systems that were obtained in cases of SnCl and SnBr. The new expected band system obtained by this method of excitation is discussed in section A of this chapter.

The band system in the region 3100-2850A has been found in the present experiment to extend over the region 3200-2850A. This system has been then photographed on the grating spectrograph and the results obtained are discussed in section B.

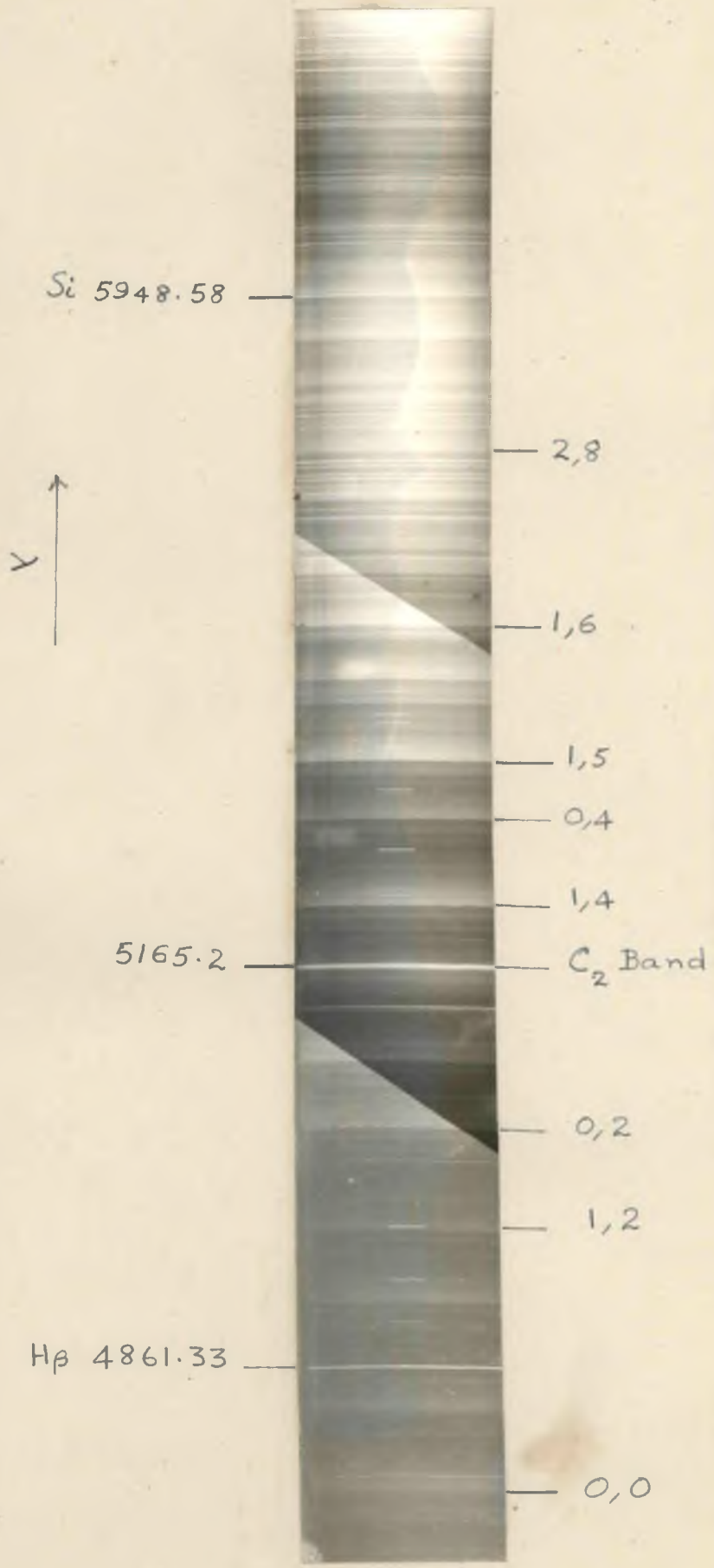

Fig. 1. The enlargement of 6200-4700A region of SiCl taken on 3-prism Spectrograph.

SECTION A

The band system in the region 6200-4700A.

The silicon tetrachloride vapour, obtained from British Drug House, was excited in the presence of argon with an uncondensed transformer discharge. The experimental arrangement is similar to that described in Chapter I. As the pressure of argon increases the continuum in the region 6300-5300A goes down in intensity and a new discrete band system appears in its place. By adjusting the pressures of argon and $SiCl_4$ it was possible to eliminate the continuum completely and obtained the new band system. However the continuum in the region 4800-3100 still persists along with the known ultraviolet band systems. The spectrum resulted in this method of excitation is a weak one and the bands are degraded towards longer wavelengths. The carl-zeiss 3-prism glass spectrograph was used to photograph this system. The spectrum was also photographed in the first order of the 3.4 meter grating spectrograph but only intense bands could be recorded in a 3 hour exposure on Ilford $H.P_3$ plates. The enlargement of this band system is shown in Fig. 1.

While the intense bands were measured with the plates taken on the grating spectrograph, less intense bands were measured from the plates taken on 3-prism spectrograph. The errors involved in the measurements

Table I contd.

I	λ air in A.U.	Assignment v' , v"	ν vac in cm^{-1}	O - C
0	5448.1	5 , 8	18350	+ .6
4	5443.3	0 , 5	18366	+ .6
2	5416.5	2 , 6	18457	-2.4
2	5390.2	4 , 7	18547	-2.4
4	5357.2	1 , 5	18661*	-0.8
1	5331.1	3 , 6	18753*	+1.4
0	5307.5	5 , 7	18836	-0.4
4	5299.4	0 , 4	18865*	0
2	5274.7	2 , 5	18953	-1.8
2	5250.3	4 , 6	19041*	+1.0
5	5217.7	1 , 4	19160*	-0.2
2	5194.4	3 , 5	19246	+0.4
1	5172.9	5 , 6	19326	-0.4
3	5162.2	0 , 3	19366	-2.4
1	5139.0	2 , 4	19454	+0.8
0	5117.5	4 , 5	19535	+0.8
4	5083.7	1 , 3	19665*	+2.4
2	5062.9	3 , 4	19746	+2.0
2	5044.1	5 , 5	19820*	-0.6
4	5030.5	0 , 2	19873*	-1.4
2	5009.6	2 , 3	19956*	+0.4
0	4990.1	4 , 4	20034	+1.4
2	4956.4	1 , 2	30170	+0.4
0	4938.2	3 , 3	20245	-1.4
1	4919.8	5 , 4	20320	+0.8

Table I contd.

I	λ air in A.U.	Assignment v' , v"	ν vac in cm^{-1}	O - C
3	4904.2	0 , 1	20385	-0.4
2	4885.6	2 , 2	20463	+0.8
1	4868.4	4 , 3	20535	0
4	4834.2	1 , 1	20680*	-1.4
4	4817.0	3 , 2	20754*	+0.6
2	4801.4	5 , 3	20821	-0.4
5	4783.3	0 , 0	20900*	-0.6
2	4766.2	2, , 1	20975	+0.6
1	4750.8	4 , 2	21043	+1.0
3	4716.7	1 , 0	21195	-0.8
0	4700.9	3 , 1	21267	+2.6

* Measured from the plates taken on the grating spectrograph.

TABLE II

THE VIBRATIONAL SCHEME FOR THE BAND SYSTEM 6200-4700A OF SiCl

v'' / v'	0	1	2	3	4	5	6	7	8	9	10	11	12	ΔG'(v'+½) Obs.	ΔG'(v'+½) Cal.
0	20900	20385	19873	19366	18865	18366	17872	17384	16898	16416					
	515	512	507	501	499	494	488	486	482						
	295	295	297	299	295	295	294	292	293	293				294·8	295
1	21195	20680	20170	19665	19160	18661	18166	17676	17191	16709	16230				
	515	510	505	505	499	495	490	485	482	479					
	295	293	291	294	292	291	292	295	291	294				292·8	293
2	20975	20463	19956	19454	18953	18457	17968	18486	17000	16524	16050				
	512	507	502	501	496	489	482	486	476	474					
	292	291	289	292	293	296	290	290	295	290				291·8	291
3	21267	20754	20245	19746	19246	18753	18258	17776	17295	16814			15872		
	513	509	499	500	492	495	482	481	481						
	289	290	288	289	288	289	286	285	287				289	288	289
4	21043	20535	20034	19535	19041	18547	18062	17580	17101	16630	16161				
	508	501	499	494	494	485	482	479	471	469					
	286	286	285	285	289	288	290							287	287
5	20821	20320	19820	19326	18836	18350	17870								
	501	500	494	490	486	480									
	515	511·7	507·2	501·2	499·2	494·2	491	484·5	482·2	478·8	472·5	469		←	ΔG''(v''+½) Obs.
	515·2	511·0	506·8	502·6	498·4	494·2	490	485·8	481·6	477·4	473·2	469		←	ΔG''(v''+½) Cal.

are estimated to be ± 4 cm^{-1} for those bands measured with the plates taken on the prism spectrograph and ± 1 cm^{-1} for those bands measured with plates taken on the grating spectrograph.

Table I contains the wavelengths and wavenumbers of the $SiCl^{35}$ bands heads taken from the average of three individual measurements. The vibrational scheme is shown in table II. The bands observed could be well represented by the equation

$$\nu = 20900.6 + 296.3v' - 1.1v'^2 - 517.3v'' + 2.1v''^2 .$$

Neither of the states involved in this transition could be identified with any of the known states of the SiCl molecule. But by the analogy with the SnCl and SnBr systems obtained by similar method of excitation, discussed in Chapters I and II, it may be said that the transition is probably $^2\Sigma \rightarrow {}^2\Sigma$.

TABLE III

Isotopic displacements in 6200- 4700A system of SiCl.

ν' of $SiCl^{37}$ in cm^{-1}	ν of $SiCl^{35}$ in cm^{-1}	v' , v''	$(\nu' - \nu)$ Obs in cm^{-1}	$(\nu' - \nu)$ Cal in cm^{-1}
16468	16416	0 , 9	52	50.8
17237	17191	1 , 9	46	47.3
17425	17384	0 , 7	41	40.9
17713	17676	1 , 7	37	37.3
17812	17776	3 , 8	36	35.8
17909	17872	0 , 6	37	33.2
18003	17968	2 , 7	35	34.0
18097	18062	4 , 8	35	32.7
18196	18166	1 , 6	30	31.7
18289	18298	3 , 7	31	30.9
18395	18366	0 , 5	29	30.4
18486	18457	2 , 6	29	28.3
18777	18753	3 , 6	24	25.1
18890	18865	0 , 4	25	24.9
19063	19041	4 , 6	22	22.0
19180	19160	1 , 4	20	21.4
19267	19246	3 , 5	21	20.3
19385	19366	0 , 3	19	19.2
19553	19535	4 , 5	18	17.2
19760	19746	0 , 2	14	13.4
20392	20385	0 , 1	7	7.4

Isotopic shift

It is known that silicon has three isotopic species, Si^{28}, Si^{29} and Si^{30}, whose natural abundance ratio is 92.:5:3. The bands corresponding to the isotopic species Si^{29} and Si^{30} will naturally be very weak and were not observed in the present experiments. Chlorine has two isotopes Cl^{35} and Cl^{37} whose natural abundance ratio is 3:1. Therefore the intensities of the bands corresponding to the more abundant molecule Si^{28} Cl^{35} should have its isotopic component corresponding to Si^{28} Cl^{37} with one third of its intensity. The measured and calculated shifts are listed in table III and the close agreement between the two suggests the correctness of the vibrational analysis.

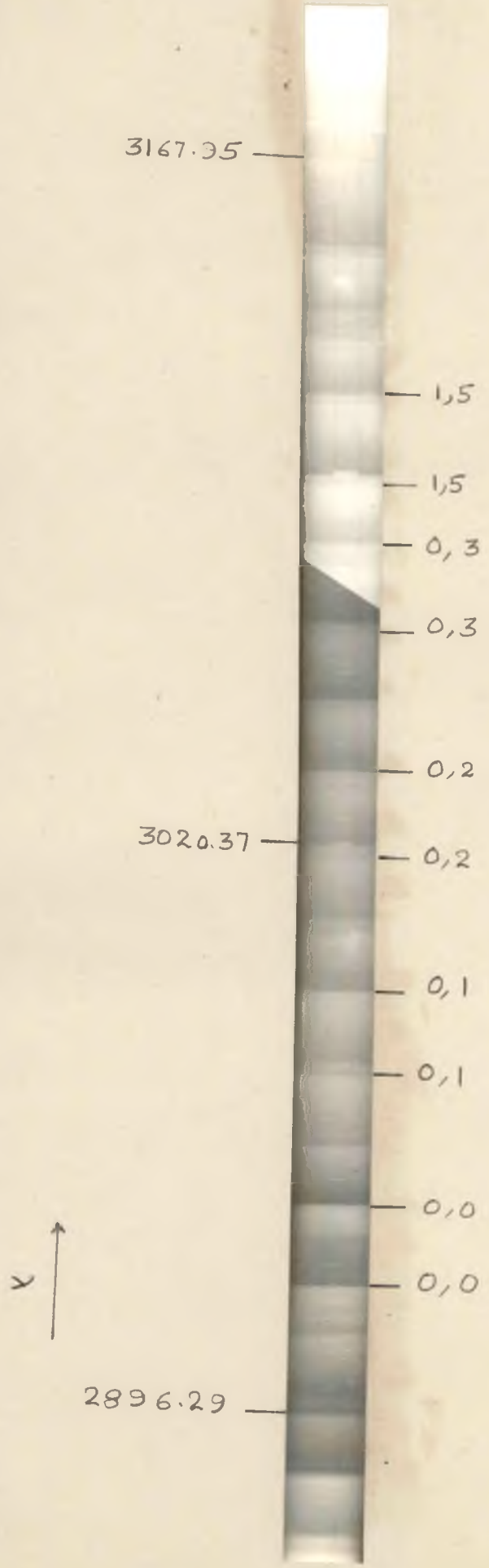

Fig. 2. The enlargement of 3200-2850A system of SiCl taken on second order grating spectrograph.

SECTION B

The band system in the region 3200-2850A.

Exciting the $SiCl_4$ vapour in the presence of argon the band system in the region 3100-2850 reported by earlier workers, has been photographed on the second order of the 3.4 meter grating spectrograph. Kodak B_{20} plates were exposed for 30 minutes and found to be satisfactory. Fig.2 shows the enlargement of the system. 45 bands were measured against 18 bands reported by earlier workers. The band system has been found to extend over the region 3200-2850A. The bands are degraded to shorter wavelength side and in general have shown P heads and Q heads.

The wavelengths and wavenumbers of the $Si^{28}Cl^{35}$ Cl^{35} band heads are tabulated in table IV. The wavelength data given by Jevons and Datta are also included for comparison. The Deslanders scheme of this system is shown in table V. All the observed bands could be well represented by the equation

$$\nu = \begin{matrix} 34184.5 \\ 33978.3 \end{matrix} + 703.1v'-4.7v'^2-532.3v''+2.1v''^2$$

As more number of bands are obtained in the present experiments than those obtained by earlier workers and as the band system is photographed on a spectrograph

TABLE IV

Datta ν_{vac} in cm^{-1}	Jevons ν_{vac} in cm^{-1}	I	v', v"	Present Experiments λ_{air} in A.U.	Present Experiments ν_{vac} in cm^{-1}	O - C in cm^{-1}
		0	1 , 7	P_1 3219.37	31053	0
				Q_1 3218.86	31058	
		1	0 , 6	P_2 3218.05	31066	-0.3
				Q_2 3217.58	31070.4	
		0	2 , 8	P_1 3200.1	31240	-1.7
				Q_1 3199.64	31244.5	
		0	1 , 7	P_2 3198.26	31258	-0.7
				Q_2 --	--	
		0	0 , 5	P_1 3197.23	31368.1	-1.2
				Q_1		
		2	1 , 6	P_1 3167.95	31557.1	-0.7
				Q_1 3167.50	31561.5	
		2	0 , 5	P_2 3166.05	31576.	+0.5
				Q_2 3165.53	31581.5	
		3	2 , 7	P_1 3149.59	31741	-1.5
				Q_1 3149.09	31746	
		3	1 , 6	P_2 3147.17	31765.4	+0.7
				Q_2 3146.63	31770.8	
		1	0 , 4	P_1 3135.06	31881.8	+0.9
				Q_1 3135.30	31885.7	
		2	2 , 7	P_2 3129.18	31948	+0.9
				Q_2 --	--	
	32064.4	2	1 , 5	P_1 3117.63	32066.4	-0.4
				Q_1 3117.14	32071.4	

Table IV contd.

Datta ν_{vac} in cm^{-1}	Jevon ν_{vac} in cm^{-1}	I	v', v"	Present Experiments λ^{*}_{air} in A.U.	ν_{vac} in cm^{-1}	O - C in cm^{-1}
	32068.7			P_2 3115.49	32088.4	-0.5
		2	0, 4	Q_2 3115.08	32092.6	
				P_1 3100.16	32247.1	-0.4
		3	2, 6	Q_1 3099.68	32247.1	-0.4
	32074.2			P_2 3097.66	32273.1	-0.8
		3	1, 5	Q_2 3097.28	32277	
32399.2	32399.1			P_1 3085.51	32399.1	-1.2
	32404.2	4	0, 3	Q_1 3085.09	32404.6	
				P_1 3083.68	32419.4	
		4	3, 7	Q_1 3083.74	32422	
				P_2 3080.37	32454.2	+0.5
		0	2, 6	Q_2 3080.03	32458	
	32577.1			P_1 3068.45	32580.3	-0.4
		5	1, 4	Q_1 3067.96	32585.5	
	32585.4					
	32608.8			P_2 3066.07	32605.6	-0.9
		5	0, 3	Q_2 3065.75	32609	
32609.5						
				P_1 3051.93	32756.7	0
		5	2, 5	Q_1 3051.42	32761.7	
	32785.3			P_2 3049.19	32786.1	-1.2
		4	1, 4	Q_2 3048.83	32790	
	32790.5					
32921.9	32922.3			P_1 3036.65	32921.5	-0.5
		7	0, 2	Q_1 3036.14	32927	
32929.8	32926.2					
				P_2 3032.91	32962.1	-0.8
		5	2, 5	Q_2 3032.43	32967.3	

Table IV contd.

Datta ν_{vac} in cm^{-1}	Jevon ν_{vac} in cm^{-1}	I	v', v"	Present Experiments λ^*_{air} in A.U.	ν_{vac} in cm^{-1}	O - C in cm^{-1}
33097.5	33097.4	7	1 , 3	P_1 3020.37	33098.9	+0.9
33104.1	33102.1			Q_1 3019.99	33103	
33127.5	33128.7	7	0 , 3	P_2 3017.75	33127.6	-0.7
33134.5	33133.2			Q_2 3017.28	33132.8	
		6	2 , 4	P_1 3004.82	33270.2	+0.1
				Q_1 3004.13	33277.8	
33306.0	33304.4	6	1 , 3	P_2 3001.76	33304.1	-0.8
33310.9	3310.4			Q_2 3001.34	33308.8	
33447.4	33448.3	9	0 , 1	P_1 2988.85	33448	-0.1
33453.8	33454.2			Q_1 2988.32	33453.9	
		1	2 , 4	P_2 2986.34	33476.1	-0.2
				Q_2 --	--	
	33621.	5	1 , 2	P_1 2973.45	33621.2	+1.1
				Q_1 2973.04	33625.8	
33656.8	33655.9	6	0 , 1	P_2 2970.48	33654.8	+0.5
	33660.0			Q_2 2969.98	33660.4	
		2	2 , 3	P_1 2958.86	33787	-0.7
				Q_1 --	--	
	33831	4	1 , 2	P_2 2955.33	33827.3	+0.6
				Q_2 2954.92	33832.2	
33977.1	33978.4	10	0 , 0	P_1 2942.2	33978.3	0
33983.7	33984.4			Q_1 2941.61	33985.1	
33185.2	34185.3	10	0 , 0	P_2 2924.4	34185.	+ 0.5
34191.4	34190.7			Q_2 2923.83	34191.7	

Table IV contd.

Datta ν_{vac} in cm^{-1}	Jevons ν_{vac} in cm^{-1}	I	V', v"	Present Experiments λ^{*}_{air} in A.U.	Present Experiments ν_{vac} in cm^{-1}	O - C in cm^{-1}
		4	2 , 2	P_1 2913.77	34309.8	+0.3
				Q_1 2913.2	34316.5	
		0	1 , 1	P_2 2910.09	34353.	+0.3
				Q_2 --	--	
		2	3 , 3	P_1 2900.22	34470.1	
				Q_1 --	--	
		4	2 , 2	P_2 2896.29	34516.8	+1.1
				Q_2 2895.74	34523.4	
34675.8	34676.9	7	1 , 0	P_1 2882.84	34677.8	
34683.6	34683.5			Q_1 2882.3	34684.4	
		3	2 , 1	P_1 2869.75	34836	+0.5
				Q_1 2869.11	34843.8	
	34884.1	0	1 , 0	P_2 2865.8	34884	+1.3
	34890.4			Q_2 65.31	34890	
		0	2 , 1	P_2 2852.77	35043.3	+1.6
				Q_2 2852.33	35048	

* The subscripts 1 and 2 refer to the two components viz. $^2\Pi_{3/2}$ and $^2\Pi_{1/2}$ of the ground state.

TABLE V

DESLANDRE'S SCHEME FOR THE BAND SYSTEM 3200-2830 OF SiCl.

v'' / v'	0	1	2	3	4	5	6	7	8	ΔG'(v+½) Obs.	ΔG'(v+½) Cal
0	33978·3 206·7 34185	530·3 33448 206·8 530·2 33654·8	526·5 32921·5 206·1 527·2 33127·6	522·4 32399·1 206·5 522·0 32605·6	517·3 31881·8 206·6 517·2 32088·4	513·7 31368·1 207·9 512·4 31576	510 31066			699·2 698·5	698·4
	699·5 699·0	698·2	699·7 699·7	699·8 698·5	698·5 697·7	698·3 697·1	699·4				
1	34677·8 206·2 34884	531 34353	525·7 33621·2 206·1 33827·3	523·2 33098·9 205·2 33304·1	518·0 32580·3 205·8 32786·1	513·0 32066·9 206·7 32273·1	507·7 31557·1 208·3 31765·4	507·4 31053 205 31258		689·3 692·6	689
		690·3	525·2 688·6 689·5	522·8 688·9	516·8 689·9 700·0	513·5 690·3 689·0	509·6 690·0 688·8	506·1 688 690	501		
2		34836 207·3 526·5 35043·3	34309·8 207 34516·8	33787 683·1	33270·2 205·9 33476·1	32756·7 205·4 514·0 32962·1	32247·1 207·1 507·9 32454·2	31741 207 506·2 31948 678·4	31240	680·8	679·6
3				34470·1				32419·4			
		530·3	525·9	522·5	516·6	513·7	509·5	505·1	501	ΔG"(v+½) Obs.	
		530·6	526·5	522·6	517·6	513·1	508·5	506·8			
		530·2	526	521·8	517·6	513·4	509·2	505	500·8	ΔG"(v+½) Cal.	

TABLE VI

Isotopic displacements of 3200-2850A system of SiCl.

ν' of $SiCl^{37}$ in cm^{-1}	ν of $SiCl^{35}$ in cm^{-1}	v' , v"	$(\nu'-\nu)$ Obs. in cm^{-1}	$(\nu'-\nu)$ Cal in cm^{-1}.
34305	34309.8 P_1	2 , 2	-4.8	-5.1
34511.5	34516.8 P_2		-5.3	
---	--- P_1	1 , 1	---	-3.1
34350	34353		-3.0	
34667.9**	34677.8 P_1	1 , 0	-9.9	-9.5
34874.6*	34884. P_2		-9.4	
34825.	34836 P_1	2 , 1	-11.0	-11.2
35022.	35043.3 P_2		-11.3	

* Observed by Jevons[3]

**;* Observed by Datta[2]

having a larger dispesion and higher resolution the vibrational constants obtained here are expected to be more accurate than those known earlier.

The observed and calculated isotopic displacements are listed in table VI.

References.

1. W. Jevons: Proc. Roy. Soc. A.106, 174, 1924.
2. A.C. Datta: Z. Phys. 78, 486, 1932.
3. W. Jevons: Proc. Phys. Soc. London, 48, 563, 1936.
4. S.N. Garg. Proc. Nat. Acad. Sci. (India), 19A, 23, 1950.

CHAPTER IV

The electronic term scheme and the stable electronic states of SiF, SiCl, SnCl and SnBr.

ABSTRACT

The electronic term scheme of the halides of silicon and tin is discussed. Electron configurations are tentatively assigned to the various observed electronic states of SiF, SiCl, SnCl and SnBr. The different stable electronic states of these molecules are listed along with their vibrational constants.

DISCUSSION

The known electronic states of SiF, SiCl SnCl and SnBr are listed in tables I-IV along with the vibrational constants. The new electronic states discussed in chapters I, II and III are also included. Though only the band systems of SnCl, SnBr and SiCl form the subject matter of this thesis, the details of the known data of SiF are also listed in table I of this Chapter. The SiF and SiCl molecules are the only molecules among the halidfs of silicon and tin for which the rotational analysis of some of the observed band systems have been worked out and therefore the nature of the involved electronic states of those band systems is well understood.

The dissociation energies as calculated according to the formula $De = \omega_e^2 / \mu \omega_e x_e$ are also listed in the tables I--IV. The values thus obtained are not expected to give accurate dissociation energies of the states. They are just included to give an some idea of the magnitude of the dissociation energies involved. These values might however be off from the accurate values by even as much as 30 percent. The probable dissociation products are not discussed here as it might not do any useful purpose to do that without knowing the dissociation energies with some certainity.

The electronic terms schemes of these different molecules are expected to be similar to one another. As an

TABLE I

SiF

STATE	T_e	A	ω_e	$\omega_e x_e$	B_e	α_e	r_e	D_e	ν_{00}	Transition	Remarks
I	(52409)										The transitions from the states E,F,G,H, and I to the ground to state X, have been observed in the region 51000 to 53500 cm^{-1} by (1)
$H^2\Sigma$	(52170)		1030	6.							
G	(52020)		1020								
F	(51770)										
E	(51224)										
$D^2\Sigma$	(47418.6		1003.2	5.64	0.625	.005	1.54	44598	47408.9 47568.2	D→X	The constants of the state D are those given by (1)
$D'^2\pi$	46606.7	0	1032.9	5.28	0.6329	0.0044		50515	23912.6	D′→A	The constants for the D′ and C′ states are
$C'^2\pi$	41964.9	16.5	1031.8	5.45	0.6376	0.0039		48835	19280.9 19264.4	C′→A	those given by (2)
$C^2\Sigma$	39513.6		891.7	6.2	0.6043	0.0067	1.570	32062	39530.7 39369.9	C→X	The constants for the state C are taken from (3).
$B^2\Sigma^+$	34561.5		1011.2	4.825	0.62707	0.00462	1.5414	55271	34556.8 34717.4	B→X	T The constants for the states B,A
									11850.8	B→A	and X are those
$A^2\Sigma$	22858.4		718.5	10.167	0.57839	0.00941	1.6049	12694	22787.4	A→X	listed by (1)
$X^2\pi$	161.8_0	161.8	857.6	4.67	0.5817	0.0056	1.600	39373			

1. Johns and Barrow Proc. Phy. Soc. 71, 476, 1958.
2. R.F. Barrow etal Proc. Phy. Soc. 73, 317, 1959.
3. R.K. Asundi and R. Samuel Proc. Ind. Acad. 3A,346, 1936.

TABLE II

SiCl

State	Te	A	ω_e	$\omega_e x_e$	B_e	α_e	r_e	D_e	ν_{oo}	Transition	Remarks
$D^2\Sigma$	44941.5		891.7	6.2				32062	45005.9	$D \rightarrow X$	The constants for the states D, C" are those given by (1)
$C''^2\Delta$	41178.4 41165.4	13	674.2	2.2				51653	41039.9 41234.8	$C'' \rightarrow X$	
$C^2\Sigma$	35530		565						35546	$C \rightarrow X$	The constants of the state C are those given by (2).
$B^2\Sigma$	34102.3		707.8	4.7	0.2782	0.0015	0.088	26648	34184.5	$B \rightarrow X$	The vibrational constants given for B state are those derived in section B of the Chapter III.
A'''	a+20911		297.3	1.1				20088	200800	$A''' \rightarrow A''$	This is the new transition observed in the present experiments discussed in section A of the III Chapter.
A''	a		519.3	2.1				32104			
$X^2\pi$	207 207 0		534.3	2.1	0.2556 0.2550	0.0016 0.0016	1.178 1.171	33985			The vibrational constants for the state X are those given in section B of the Chapter III. The rotational constants for the states B and X are those given by (3).

1. W. Jevons. Proc. Phys. Soc. (Lond.) 48, 563, 1936.
2. S.N. Garg. Proc. Nat. Acad. Sci. 19A, 24, 1950.
3. I.E. Ovcharenka and etc. optics and spectroscopy, 8,393,1960.

TABLE III

SnCl

State	Te	A	ω_e	$\omega_e x_e$	De	ν_{oo}	Transition	Remarks
$D'^2\Pi$	43724.0 43656.1	67.9	392.8	1.4	27552	41383.8 43676.2	$D' \leftarrow X$	The constants for the state D' are those given by (1)
$B^2\Sigma$	33585.5		432.5	1.2	38970	31265 33625	$B \rightleftarrows X$	The higher energy components of the B and $A \longrightarrow X$ transitions have been observed in absorption by (1).
$A'''^2\Sigma$	a•19417.3		232.8	0.9	15054	19354	$A''' \rightarrow A'$	This is the new transition discussed in section A of Chapter I.
$A''^2\Sigma$	a		347.4	0.7	44698			
$A'^2\Delta$	28966.4 28692.3	274	303.3 300.8	4.0 3.7	5749 6113	26580 28666	$A \rightleftarrows X$	The vibrational constants for the states X, A' B given here, are the modified vibrational constants taken from Chapter I; Sections B and C.
$X^2\Pi$	2360 0	2360	354.3 353.6	1.0 1.2	31382 26049			

1. C.A. Fowler Jr. Physic. Rev. 62, 141, 1942.

TABLE IV

SnBr

State	Te	A	ω_e	$\omega_e x_e$	De	ν_{oo}	Transition	Remarks.
$B\,^2\Sigma$	(33218.2)					30627.5 33094.5	$B \longrightarrow X$	The upper state with a single level =0 has been observed by (1) and so ω_e and $\omega_e x_e$ values were not reported.
$A'''\,^2\Sigma$	a +18715.5		164.1	0.9	7480	18675	$A''' \longrightarrow A''$	this is the new transition discussed in Chapter II.
$A''\,^2\Sigma$	a		247.2	0.48	33576			
$A'\,^2\Delta$	27067. 28695.1	371	163.6 169.1	6.8	10.51	24557.9 26654.3	$A' \longrightarrow X$	The constants for the states B, A and X and those given by (1)
$X\,^2\Pi$	2467 0	2467	247.7	0.62	24740			

1. W. Jevons and L.A. Bashford. Proc. Phy. Soc. (Lond.) 49, 554, 1937.

TABLE V

The electronic Term Scheme* of the halides of Silicon and Tin.

Ratio of the bonding to antibonding electron** among the out outer 11 electrons.	Electron Configuration										Electronic States
	$z\sigma$	$y\sigma$	$x\sigma$	$w\pi$	$v\pi$	$u\sigma$	$s\sigma^x$	$p\sigma^x$	δ		
7:4	2	2	1	4	2						$^2\Sigma^+$, $^2\Sigma^-$ $^2\Delta$ $^4\Sigma^-$
(9:2)	2	1	2	4	1		1				$^2\pi$, $^2\pi$, $^4\pi_\gamma$
(8:3)	2	2	1	4	1		1				$^2\pi$, $^2\pi$, $^4\pi_\gamma$
(9:2)	2	2	2	4					1		$^2\Delta$
(8:3)	2	2	2	3	1		1				$^2\Sigma^+$, $^2\Sigma^+$, $^2\Sigma^-$, $^2\Sigma^-$, $^2\Delta$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-$, $^4\Delta$.
(9:2)	2	2	2	4				1			$^2\Sigma^+$.
(9:2)	2	2	2	4			1				$^2\Sigma^+$
8:3	2	1	2	4	1	1					$^2\pi$, $^2\pi$, $^4\pi_\gamma$
7:4	1	2	2	4	2						$^2\Sigma^+$, $^2\Sigma^-$, $^2\Delta$, $^4\Sigma^-$
8:3	2	1	2	4	2						$^2\Sigma^+$, $^2\Sigma^-$, $^2\Delta$, $^4\Sigma^-$
7:4	2	2	1	4	1	1					$^2\pi$, $^2\pi$, $^4\pi_\gamma$
7:4	2	2	2	3	1	1					$^2\Sigma^+$, $^2\Sigma^+$, $^2\Sigma^-$, $^2\Sigma^-$, $^2\Delta$, $^2\Delta$, $^4\Sigma^+$, $^4\Sigma^-$, $^4\Delta$
8:3	2	2	2	4		1					$^2\Sigma^+$
7:4	2	2	1	4	2						$^2\Sigma^+$, $^2\Sigma^-$, $^2\Delta$, $^4\Sigma^-$
7:4	2	2	2	3	2						$^2\pi_i$, $^2\pi_\gamma$, $^2\pi$, $^2\phi_i$, $^4\pi_i$
8:3	2	2	2	4	1						$^4\pi_\gamma$

* The Term scheme is based on Mulliken's article.

** The electrons $z\sigma$, $x\sigma$ and $w\pi$ are bonding electrons while $y\sigma$, $v\pi$ and $u\sigma$ are antibonding. The electrons $s\overset{x}{\sigma}$, $p\overset{x}{\sigma}$ and δ are those probably with appreciable bonding capacity. The values in the parantheses have been calculated with the assumption that $p\sigma^x$, $s\sigma^x$ and δ have appreciable bonding capacity.

TABLE VI

State	Configuration	SiF		SiCl		SnCl		SnBr	
		Te	ω_e	Te	ω_e	Te	ω_e	Te	ω_e
$D'^2\pi$	$(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(v\pi)(s\sigma^*)$	46606.7	1032.9			43724.0 43656.1	392.8		
$C''^2\Delta$	$(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(\delta)$			41178.4 41165.4	674.2				
$C'^2\pi$	$(z\sigma)^2(y\sigma)(x\sigma)^2(\omega\pi)^4(v\pi)(s\sigma^*)$	41964.9	1031.8						
$C\ ^2\Sigma$	$(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(p\sigma^*)$	39513.6	891.7	35530	565				
$B\ ^2\Sigma^+$	$(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4 s\sigma^*$	34561.5	1011.2	34102.3	707.8	33585.5	432.5	33218.2	
$A''^2\Sigma$	$(z\sigma)^2(y\sigma)^2(x\sigma)(\omega\pi)^4 v\sigma^2$			a+20911	297.3	a+19417	232.8	a+18715	164.1
$A''\ ^2\Sigma$	$(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4 v\sigma$			a	519.3	a	347.4	a	247.2
$A'\ ^2\Delta$	$(z\sigma)^2(y\sigma)^2(x\sigma)(\omega\pi)^4(v\pi)^2$					28966.4 28692.3	303.3 300.8	27867 26695.1	163.6 169.1
$A\ ^2\Sigma^+$	$(z\sigma)^2(y\sigma)^2(x\sigma)(\omega\pi)^4(v\pi)^2$	22858.4	718.5						
$X\ ^2\pi$	$(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(v\pi)$	161.8 0	857.6	207 0	534.3	2360 0	354.3 353.6	2467 0	247.7

Note: The states B, D, and probably H in SiF are regarded as belonging to Rydberg series by Johns and Barrow. (Proc. Phys. Soc. 73, 476, 1958.) If so, it is possible that B and D states of SiCl may also form Rydberg series.

example one can take up the SiCl molecule. The atomic configuration of silicon is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$ and that of chlorine is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^5$. Of the different electrons the $3s^2\ 3p^2$ electrons of silicon and $3s^2\ 3p^5$ of chlorine may be taken to represent outer 11 electrons of the SiCl molecule.

Following Mulliken's[1,2] notation the lowest electronic configuration of the SiCl molecule in terms of the 11 outer electrons may be represented as

$$(z\sigma)^2\ (y\sigma)^2\ (x\sigma)^2\ (w\pi)^4\ v\pi$$

This configuration represents the configuration of the outer 11 electrons of the ground states of all these different monchalides of silicon, tin, carbon and germanium. For example in the case of SiCl $(z\sigma)$ represents the bonding orbital of the type $(3s\sigma\ si + 3s\sigma\ cl, \sigma)$ and $(y\sigma)$ represents the antibonding orbital of the type $(3s\sigma\ si - 3s\sigma\ cl, \sigma$ cl,), $(w\pi)$ and $(v\pi)$ represent bonding and antibonding orbitals of the type $(3p^{\pi}\ si + 3p^{\pi}\ cl, \pi)$ and $(3p^{\pi}\ si - 3p^{\pi}\ cl, \pi)$ cl,). $(x\sigma)$ represents a bonding orbital of the type $(3p\sigma\ si + 3p\sigma\ cl, \sigma)$.

It may be noted that Johns and Barrow[3] take the configuration of the lowest state as $(z\sigma)^2(y\sigma)^2(w\pi)^4(x\sigma)^2(v\pi)$. Though for lighter molecules $(w\pi)$ has lower energy than $(x\sigma)$, it is expected that for the type of the molecules that are being considered here, $w\pi$ will have higher energy than $x\sigma$. For molecules upto C6, $w\pi$ is known[1,2] to be

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lower than $x\sigma$, while for molecules from NO onwards $w\pi$ is higher than $x\sigma$.

The different excited states that one gets from some of the different excited configurations are given in Table V. Some of these states can be expected to be repulsive. The ratio of bonding and antibonding electrons is given for each configuration. Assuming that the relative stabilities and therefore the vibrational frequencies of the different states are dependent upon this ratio, one can proceed to assign tentatively the electronic configuration to the different observed excited states of the molecule. Such a procedure has been followed and the tentative assignments of the electronic configuration to the observed states are given in table VI for all the molecules considered here.

One of the lowest excited configurations which gives a $^2\Sigma^+$ state is probably $(z\sigma)^2\ (y\sigma)^2\ (x\sigma)\ \ (w\pi)^4\ (v\pi)^2$. This may be expected to be the configuration of the $^2\Sigma^+$ state designated as A in SiF and SnF. One cannot rule out the possibility of the configuration $(z\sigma)^2\ (y\sigma)^2\ (x\sigma)^2\ (w\pi)^4$ $(u\sigma)$ being responsible for this state. However as the observed ω value of the $A^2\Sigma^+$ states in SiF is much lower than that of the corresponding ground state, it is expected that the configuration of the $A^2\Sigma^+$ state will have a smaller number of bonding electrons than the ground state. $(z\sigma)^2\ (y\sigma)^2\ (x\sigma)\ (w\pi)^4\ (v\pi)^2$ is therefore assigned to be $A^2\Sigma_u^-$ state of SiF at 22858.4 cm^{-1} The analogous state[3]

in SnF is at 20137.8 cm^{-1}. The same configuration gives also a $^2\Delta$ state and therefore this configuration is also assigned to the low lying A'$^2\Delta$ states of SnCl and SnBr. Another alternative configuration $(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^3(v\pi)(u\sigma)$ could also be responsible for this $^2\Delta$ state and therefore this alternative is also included in the table.

The B $^2\Sigma^+$ states of SiF SiCl and SnCl have much larger vibrational frequencies than the corresponding ground state vibrational frequencies. The lowest electronic configuration which may give such a state is $(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4(s\sigma^x)$ where $(s\sigma^x)$ is taken to be an excited orbital. For example in SiCl this $s\sigma^x$ will be of the type $4s\sigma$. The electronic configurations involving such σ^x orbitals in I_2, Icl etc. are known[4,5] to give excited states with larger vibrational frequencies than the ground state indicating that they have appreciable bonding capacity. Such a configuration has been attributed by Johns and Barrow to the $B^2\Sigma^+$ state of SiF which appears to be reasonable. The B $^2\Sigma^+$ states of all the molecules concerned in this chapter are thus attributed to the electron configuration of the type $(z\sigma)^2(y\sigma)^2(x\sigma)^2(\omega\pi)^4\sigma^x$ The corresponding B $^2\Sigma^+$ state of SnF lies at 34107.9 cm^{-1} and that of SiBr at 33571.0 cm^{-1}. The B, D and H states of SiF are taken as Rydberg series by Johns and Barrow, and they are

indicated as such in the table. The B and D states of SiCl may also be probably taken as a Rydberg series. A configuration of the type $(z\sigma)^2 (y\sigma) (x\sigma)^2 (\omega\pi)^4 (v\pi)(\delta\sigma^*)$ is probably reasonable to give the two $^2\pi$ excited states of SiF(C′ and D′) having vibrational frequencies nearer to one another but much larger than vibrational frequency of the ground state. The observed $^2\pi$ state of SnCl is probably analogous to the D′ $^2\pi$ state of SiF. The $^2\Delta$ state in SiCl which is designated as C″ and which has again a larger ω value than the ground state is probably due to a configuration of the type $(z\sigma)^2 (y\sigma)^2 (x\sigma)^2 (\omega\pi)^4 (\delta)$ in which δ is bonding orbital. The C $^2\Sigma^+$ state of SiCl at 35530 cm^{-1} and the C state of SiF if it is also a $^2\Sigma^+$ state may probably arise in the configuration of the type $(z\sigma)^2 (y\sigma)^2 (x\sigma)^2 (\omega\pi)^4 (p\sigma^*)$. In SiCl and SiF the $p\sigma^*$ will probably be like 4 $p\sigma$. The nature of the state of SiF is said to be a questionable and therefore the assignment also is to be taken in the same manner.

The states of the new systems in SiCl, SnCl, and SnBr have vibrational frequencies nearly equal to those of the ground states, while the upper states have low vibrational frequencies. This suggests that the lower states of the new systems have probably the same number of bonding electrons as the ground state while the upper states will have a smaller number. The new systems, if

they are due to $^2\Sigma^- \rightarrow {}^2\Sigma^+$ may then be because of a transition of the type,

$$(z\sigma)^2 (y\sigma)^2 (x\sigma) (\omega\pi)^4 (u\sigma)^2 \cdots {}^2\Sigma^+ \longrightarrow$$
$$(z\sigma)^2 (y\sigma)^2 (x\sigma)^2 (\omega\pi)^4 (u\sigma)\ {}^2\Sigma^+$$

The new states are designated as A" and A"' in the tables. The letter designations (ABC etc.) of all the different states of SiF are the same as those used by Johns and Barrow[6,3]. The analogous states in the different molecules considered here are designated by like same letters.

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